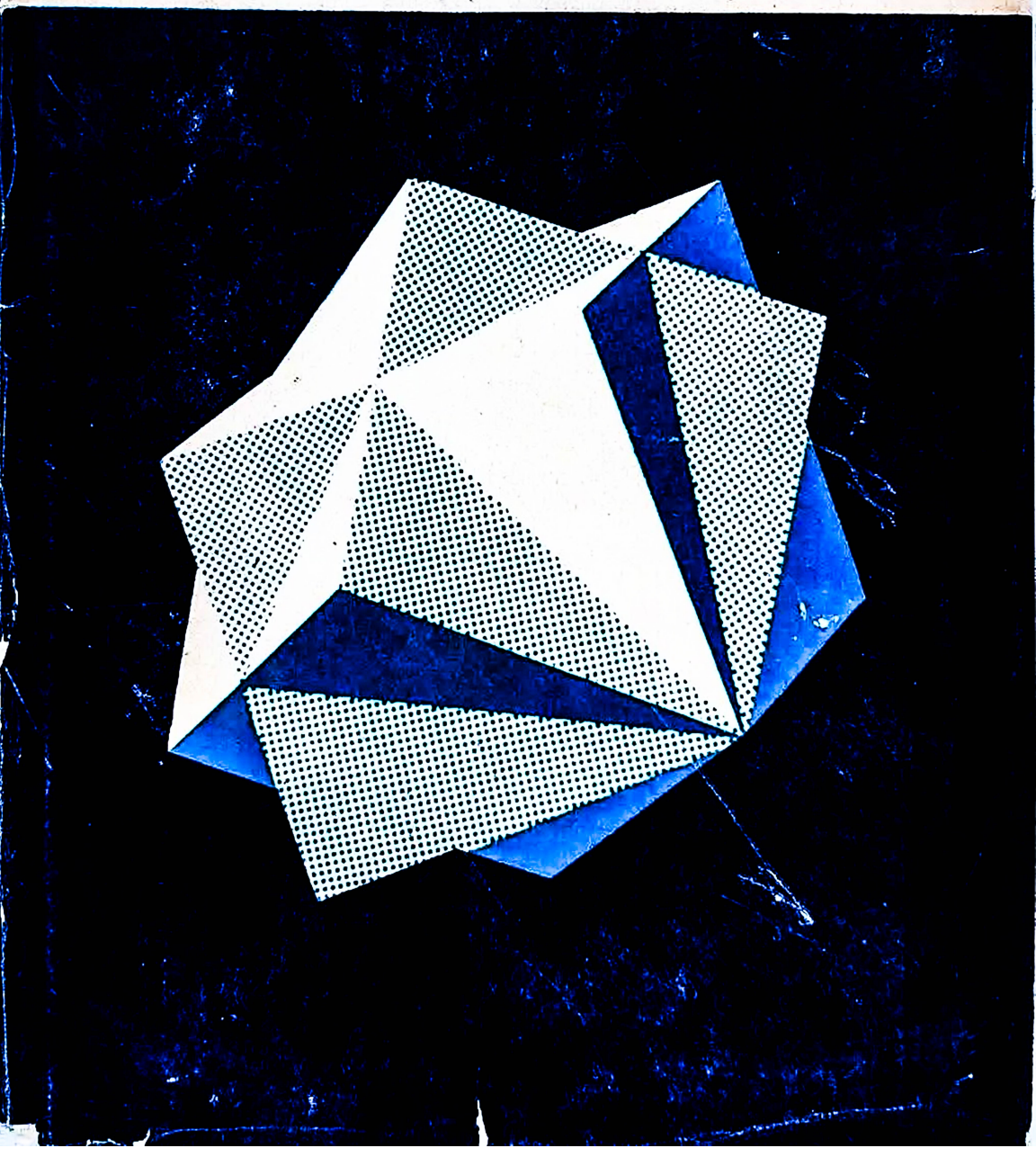
Y. FLINT

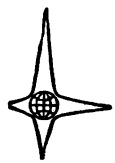
Essentials of crystallography



ABOUT THE BOOK

This is the second English edition of the standard Soviet textbook on crystallography for university faculties of geology and mining. It sets out the essentials of the subject (the theory of crystals), indicates its connections with other disciplines, and explains the basic laws governing the development, growth, structure and constant symmetry of crystals, and the laws of constancy of angle, whole numbers, zones, and crystallographic limits. The forms of crystal growth are reviewed, a survey given of the simple forms by classes, and the most important crystal properties described. The book also includes tables relating the notation for the simple forms of crystal used in the USSR to those used in other countries.

Y. FLINT ESSENTIALS OF CRYSTALLOGRAPHY



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МОСКВА

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by

Prof. E. FLINT

◇

Translated from the Russian

by

V. SNIGIREVSKAYA

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TO THE READER

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На английском языке

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CHAPTER I

General

CRYSTALLOGRAPHY AND ITS RELATIONSHIP WITH OTHER BRANCHES OF SCIENCE

The word "crystal" is of Greek origin, it is formed from two words: κρυοζ—cold, and στελλεσθαι—to congeal, and means "congealed by cold". The Greeks, as well as the scholars of later ages (Stensen, 1638-1686), applied the word κρυζταλλοσ to rock crystal, as they believed it to have been formed from ice crystals. Some Greek philosophers thought that ice would always change to a specific form, stable at normal temperature, if it was kept for some time at an extremely low temperature, i.e., if it was "congealed by cold".

Crystallography is the science of crystals in their development and growth, their external form, internal structure, and physical properties.

For a very long time crystallography was a part of mineralogy, an introduction to it. At the end of the 19th century, however, it became an independent discipline for several reasons the most important of which were the following.

1. With the progress in chemistry, especially in organic chemistry, it became evident that a tremendous number of substances, having nothing in common with minerals, had a crystalline structure.

2. Crystals, or more precisely, crystalline substances, are very widespread. The overwhelming majority of bodies and objects surrounding us have a crystalline structure. The earth and the stones we walk on, the walls and roofs of our houses, even wood*—all this has a totally or partly crystalline structure, often a very complicated one.

3. Crystals have highly diversified specific properties.

The diagram in Fig. 1 gives a general idea of the position of crystallography among allied branches of science. The arrows show the direction of relative dependence and mutual usefulness. For instance, crystallography makes extensive use of mathematics,

* Wood consists mainly of cellulose $(C_6H_{10}O_5)_{12}$, whose elongated molecules form a crystal structure.

but adds very little to it. Just the reverse is the case with metallography (the definitive study of the structure of metals) and petrography—the study of rocks. There is a close interrelationship between crystallography, on the one hand, and physics, chemistry, and mineralogy, on the other.

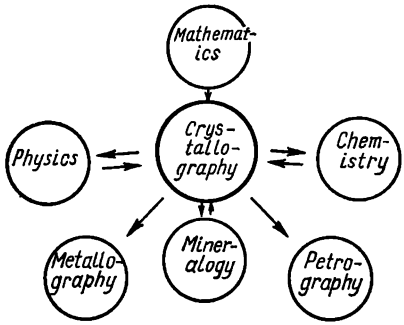


Fig. 1. Relationship of crystallography with other sciences

Crystallography began using mathematics extensively a very long time ago. It soon became evident that some branches of mathematics, especially important for crystallography (e.g. the theory of the external form of polyhedra, the geometry of symmetry, the theory of the filling of a plane and space with figures), were not sufficiently developed and did not appear of special interest to mathematicians. Therefore, the crystallographers did their own work in these branches of mathematics, with great success in some cases; this is especially true of E. S. Fedorov, one of the greatest crystallographers in the world.

AN OUTLINE OF THE DEVELOPMENT OF CRYSTALLOGRAPHY

A very long time ago, in studying crystals researchers became convinced that one of the features of a crystalline substance was the regular periodicity, or retlcular nature, of its structure.

The first reference to the regular arrangement of spherical material particles that make up a crystal can be found in the works of the famous astronomer J. Kepler (1619) and of the inventor of the microscope R. Hooke (1665). The Dutch scientist, C. Huygens in 1690 made a study of the optical properties of calcite crystals ($CaCO_3$) and put forward a hypothesis explaining these properties by the regularity of the internal structure of the crystalline substance. He visualized a crystal as consisting of material particles of a definite shape (Fig. 2), specific for each substance.

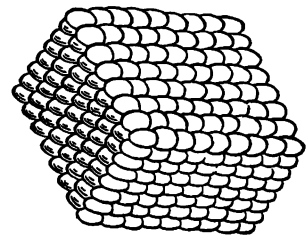


Fig. 2. Structure of calcite after C. Huygens

Some time earlier, in 1669, Nicholas Stensen (Nicolaus Steno) discovered the first basic law of crystallography—*the law of constancy of angle*. At about the same time E. Bartholinus discovered

birefringence in Iceland spar crystals and laid the foundation of crystal optics.

M. V. Lomonosov (1711-1765) developed the corpuscular theory of the structure of matter. He believed corpuscles to have a spherical shape. Mentally building up crystals from the corpuscles, Lomonosov explained the sectional shape of "crystalline figures" as being square for common salt and hexagonal for nitre. In the same way he explained the parallel arrangement of diametrically opposite faces. Lomonosov's theory made it possible to give a perfectly correct explanation of the law of constancy of interfacial angles: successive superposition of the layers of corpuscles during crystal growth results in the crystal faces being successively translated parallel to themselves.

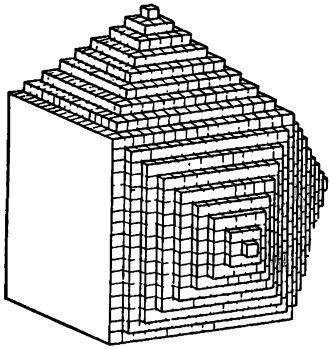


Fig. 3. Development of a new face as a result of omission of structural units—cubelets

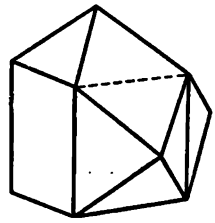
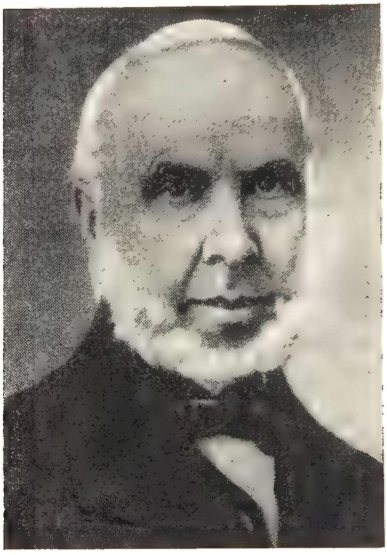


Fig. 4. New faces tangent to steps shown in Fig. 3

Unfortunately, very few of Lomonosov's laboratory notes have survived to our day. We can see from his detailed programs of crystal studies that he was engaged in the investigation of crystal form as well as of the physical properties of crystals: measurements of angles, refraction of light, specific gravity, cohesion forces, hardness, and electrical properties manifested in luminescence (triboluminescence, as we call it today) and the ability to attract light particles.

Lomonosov devoted much attention to the process of crystallization. Instructions on methods of crystallization by rapid or slow cooling, evaporation in flat or tall vessels in the presence or absence of air in the solutions have been found in his works. He even raised the problem of the rate of crystallization in "electrified solutions"—a problem which still remains unsolved.

In 1774 R. J. Haüy discovered the second basic law of crystallography—*the law of whole numbers*, better known under the name of *Haüy's law of rational indices*. Haüy observed that calcite crystals split in a definite manner and produce plane splendent surfaces



W. H. Miller

along the direction of splitting (the phenomenon of cleavage). Haüy assumed that the molecules making up the crystal had a permanent shape of parallelepipeds. When a crystal is built up of such molecules (Figs. 3 and 4), the spatial position of each of its faces can be denoted by three whole numbers.

In the first decade of the 19th century work was started on systematic measurement of interfacial angles of natural crystals, i.e., minerals. At that time crystallography was closely associated with mineralogy and was a part of it. Many mineralogists (Weiss, Neumann, Naumann, and Miller) were engaged in measuring crystals, mainly minerals. W. H. Miller was the first to use methods of analytical geometry in crystallography. He evolved a rational system of symbols for the designation of faces by means of indices.

Crystals were first measured with contact goniometers, and later with reflecting goniometers.* The first type of this instrument was invented by Carangeot in 1782, and the second by Wollaston in 1809.

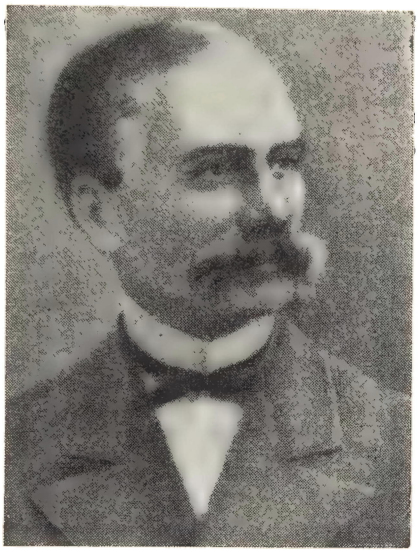
In Russia measurements of crystals were made by N. I. Koksharov (1818-1892), P. V. Eremeyev (1830-1899), M. V. Erofeyev (1839-1889), and others. The most thorough and accurate goniometric measurements were made by N. I. Koksharov. He studied a great number of minerals from Russian deposits. The results of his crystallographic measurements are still valid today and are often quoted in modern textbooks and handbooks on mineralogy.

At the beginning of the 19th century the fundamental principles of the law of symmetry of crystals were laid down, the zone law was discovered, and the classification of crystals was worked out. All the possible crystal classes were first derived by Hessel in 1830. In 1867 the Russian scientist Academician A. V. Gadolin (1828-1892) derived geometrically, with perfect accuracy, the 32 types of symmetry of crystals.

The study of artificial crystals began in the second half of the 19th century. Crystallography gradually branched away from mi-

* From the Greek words γωνια—angle, μετρο—to measure.

neralogy and drew closer to physics and chemistry, finally becoming an independent branch of science. The number of workers in this field grew rapidly. The laws of chemical crystallography were discovered, as well as isomorphism and polymorphism, and the optical properties of crystals were studied in great detail. By the end of the 19th century geometrical theories of crystal structure had been evolved.



A. V. Gadolin

The latest stage in the development of crystallography began in 1912.

For a number of years nobody could prove experimentally the validity of the reticular theory of crystal structure. At the end of the 19th century some workers even began to doubt the validity of the theory of the molecular structure of matter, and many scientists avoided referring to the reticular nature of crystal structure. Only in 1912 M. Laue succeeded in supplying an experimental proof of the validity of the reticular theory.

A new type of radiation was discovered by W. K. Röntgen in 1895. The unusual properties of these rays (called X-rays by Röntgen) remained unexplained for a long time. Some physicists thought them to be electromagnetic vibrations with a very short wavelength, others believed that they were emission-type rays (i.e., due to the effluence of minute material particles) because no tests resulted in reflection, refraction, or interference phenomena. The finest diffraction gratings that could be produced artificially had no effect on the X-rays.

Laue decided to use a natural diffraction grating—a crystal—believing that gratings made by human hands were too coarse for the supposedly very short waves of X-rays. If the theory of the reticular structure of crystalline substance was true, a crystal would be so fine three-dimensional grating that it could cause interference of the assumed ultra-short waves of X-rays. Thus, the investigator had to solve two problems at once: (1) to establish the nature of X-rays, and (2) to prove experimentally the validity of the reticular theory of crystal structure. The results of this experiment provided

E. S. Fedorov

the solution to both these problems and opened up new avenues for further development of crystallography, physics, and chemistry.

Once this discovery was made, many prominent physicists and crystallographers began using X-rays for the study of crystal structure and developed a number of original research methods.

In the second half of the 19th century two outstanding crystallographers appeared in Russia: E. S. Fedorov and G. V. Wulff.

E. S. Fedorov (1853-1919) made a number of remarkable works on geometrical crystallography and on the theory of crystal structure. He evolved the theory of parallelohedra, derived the 230 space groups, and discovered the law of crystallographic limits.

In 1889 Fedorov devised a two-circle goniometer. Goniometers of this type have become highly important in crystallographic work.

The Fedorov stage for optical examination of crystals is particularly popular. There is not a single petrographic laboratory where this stage is not used.

Towards the end of his life Fedorov completed his formidable work *Das Kristallreich* (The Kingdom of Crystals), which is a manual for the determination of crystals. In this fundamental work Fedorov showed that the composition of crystals could be determined from their external form. He evolved a new method for the determination of crystals—crystallochemical analysis, which is the pride of Russian science.

G. V. Wulff (1863-1925) was engaged in physical crystallography, he carried out some highly important investigations into the theory of crystal growth, of liquid crystals, and also devised the simplest and easiest method of calculation of the constants of crystals and of face symbols. For graphical calculations he devised a net of equatorial type. With the aid of this net and with sufficient experience it is possible to obtain an accuracy of $\pm 15'$. The Wulff net is now universally used as the most rational and convenient tool. It should be noted that it is used not only in crystallographic work,

but also in other fields of knowledge: astronomy, navigation, and even in mining (for the determination of the strike and dip of beds and veins from the angle of outcrops).

Soon after the discovery by Laue of the X-ray method of crystal-structure analysis, Wulff, simultaneously with W. H. Bragg and W. L. Bragg, but quite independently, worked out the principal analysis formula which is now called the Bragg-Wulff formula.

G. V. Wulff

A. V. Shubnikov, who worked in various branches of crystallography, was a pupil of Wulff's. He wrote some outstanding works on the symmetry of crystals, the processes of crystal growth, crystal optics, and the piezoelectric properties of crystals. Shubnikov introduced crystallography into industry and engineering. He founded within the Academy of Sciences an Institute for Crystallographic Research—the only one of its kind in the world.

The foremost specialist in the field of crystal chemistry in the Soviet Union is Academician N. V. Belov. He has derived polyhedra that correspond to various coordination numbers. The concept of close-packed structures, which he has worked out in great detail, facilitates considerably structural studies of ionic crystals and makes it possible to introduce corrections into some earlier works.

THE PRINCIPAL SPECIFIC PROPERTIES OF CRYSTALLINE SUBSTANCES

1. We often see in mineralogical collections large beautiful crystals, sometimes with plane and mirror-smooth faces. They were never ground or polished but are the outcome of a natural process. Minute crystals, visible only through a magnifying glass or with the aid of a microscope, are also frequently well faceted.

Crystals are bounded by plane faces, straight edges, and angles. The relationship between these elements can be expressed by the formula:

$$f+c=e+2,$$

where f, c and e are the numbers of faces, angles and edges respectively.

Crystal faces are arranged in zones. A *zone* is a complement of faces intersecting along parallel edges. A *zone axis* is a line running parallel to the zone edges.

There is a system in positioning of the faces:

(a) the angles between the corresponding faces of the crystals of the same chemical compound are constant;

(b) when the position of the faces in space is related to three definitely selected coordinate axes, the position of any face can always be expressed by three simple whole numbers.

2. A study of the physical properties of crystals shows that in the general case these properties are different for different directions,

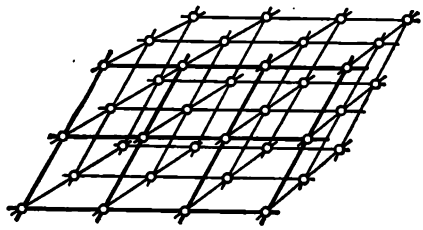


Fig. 5. Space lattice

i.e., the crystals are *anisotropic*. For instance, the hardness, heat conductivity, elasticity, and other properties of crystals vary with the direction of measurement.

3. In some directions the properties of crystals are the same; the arrangement of such similar directions reveals a highly diverse and often complex symmetry.

4. As regards light, most crystals behave in a peculiar manner: any incident ray of light is resolved into two plane-polarized rays with different refractive indices, i.e., the rays travel through a crystal medium at different velocities.

The observed characteristics of crystals can be easily explained if we assume a regular *latticed* (*reticular*) *structure* for crystal substances, without reference to the nature and shape of the material particles making up the crystal. Therefore, the structure of a crystal is usually represented diagrammatically in the form of a space lattice (Fig. 5). It can be visualized as a system of an infinite number of equidimensional parallelepipeds stacked up in a parallel arrangement without any gaps between them. The coigns of the parallelepipeds, or random points chosen in each of them in precisely the same spot, constitute the space lattice. The points are called *nodes*,

the lines drawn through them are *rows*, and planes defined by three nodes from different rows are *plane nets*. The parallelepipeds themselves, with nodes in their coigns, are usually called *unit cells* of the lattice. Such diagrammatic representation affords an easy explanation of many, if not all, specific features of crystals.

The development of plane faces and straight edges in a crystal is quite natural, if the base of its structure is a reticular-type skeleton, i.e., a space lattice. Each edge should correspond to a row. The rows are infinitely varied in number and direction, each edge being defined by two points—nodes of the lattice. The faces correspond to plane nets; the position of each face is defined by three points—nodes from different rows.

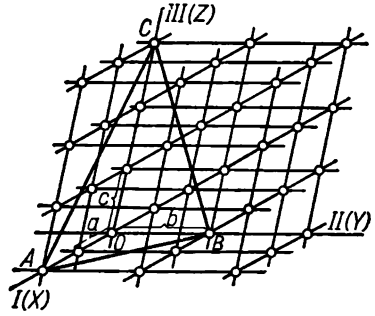


Fig. 6. Face *ABC* cuts a whole number of intercepts on coordinate axes

Since crystals of the same substance have the same lattice at similar temperature and pressure, it may be inferred that the angles between the corresponding faces are constant. When two similar lattices are placed in a parallel position, it can easily be seen that the mutual inclination of two corresponding plane nets must always be the same, quite irrespective of the size of the crystals.

The position in space of any plane net, and accordingly of any crystal face, can always be defined in terms of three whole numbers, provided that the directions of three rows of a lattice serve as coordinate axes, and the segments between nodes in the rows serve as units of measurement. The diagram in Fig. 6 shows that the position of the *ABC* face with respect to the coordinate axes *I*, *II*, *III*, or *OX*, *OY*, *OZ*, can be expressed as the number of segments *a*, *b*, and *c*, i.e., $2a : b : 3c$, or simply $2 : 1 : 3$.

The reticular skeleton of the structure accounts for the anisotropy of crystals, since parallel directions in a lattice are similar, and nonparallel ones are dissimilar.

The diversity of the symmetry of external forms and of physical properties of crystals is also easily explained if parallelepipeds with different angles and similar or different edges are taken as the primary structural units of the lattice.

CRYSTALLINE AND AMORPHOUS SUBSTANCES

It follows from the above that as a first approximation crystals can be described as *solids with a reticular structure.* A solid without such a structure is called *amorphous.* The properties of amorphous bodies are distinctly different from those of crystalline substances. At first this difference seemed to be so obvious that there was never

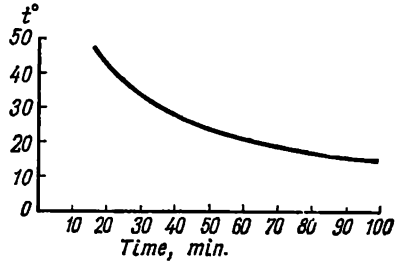


Fig. 7. Cooling curve for an amorphous substance

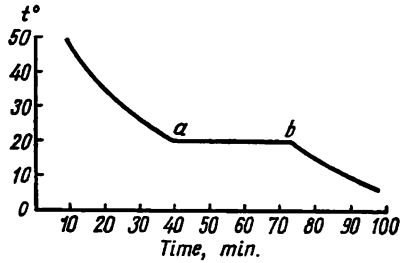


Fig. 8. Cooling curve for a crystalline substance

any doubt about the substance belonging to one or the other type. As the methods of investigation improved, however, it was found that many bodies formerly believed to be amorphous were actually wholly or partly crystalline. The clear-cut boundary disappeared. The term "amorphous" has been adopted from the Greek and means "shapeless". When a solid is described as "amorphous" it means that the substance has no natural geometrical form or regular internal structure. The particles of the substance are arranged at random as in a liquid. Therefore, solid amorphous substances are regarded as supercooled liquids. The most important features of an amorphous substance are the following: (1) the absence of a definite melting point; (2) isotropy, i.e., similar properties in different directions.

An amorphous substance differs from a crystalline one mainly in the nature of the cooling curve. Figures 7 and 8 are records of the time and temperature of cooling of two melted substances. Temperature is plotted in degrees Centigrade along the ordinate axis, and time in minutes—along the abscissa. The curve for an amorphous substance (Fig. 7) is smooth, while the curve for a crystalline substance (Fig. 8) has breaks (*a* and *b*) which correspond to the beginning and the end of the process of crystallization.

As can be seen from the curve in Fig. 8, the melted crystalline substance had been cooling gradually down to 20° C (point *a*) for about 40 minutes. Crystallization started at that temperature, and for about 30 minutes the curve ran parallel to the abscissa—the temperature remained at the level of 20° C. Crystallization was completed 73 minutes from the beginning of the experiment (point *b*) at which point uniform cooling began again. In spite of constant radiation of heat into the ambient space, the temperature remained at a constant level during crystallization. What was the reason for this? The process of crystallization is accompanied by some liberation of energy, which compensates for the loss of heat and causes the temperature to remain constant.

The above concept of the crystalline state developed in the second half of the last century. At the earlier stages of the development of crystallography only natural or artificial formations intricately and beautifully faceted were believed to be crystals. Of course, as long as crystals occurred largely among minerals, crystallography remained a branch of mineralogy.

The initial connection with mineralogy left a peculiar imprint on crystallography, which survived for a considerable time. Crystallography was the concern of mineralogists who subjected it to the demands of their own discipline. Later, when the relationship between the physical properties of solids and their reticular structure became evident, as well as the relationship between this structure and chemical composition, crystallography attracted the attention of physicists, chemists and metallographers.

CHAPTER II

Formation and Growth of Crystals

Crystals appear in the course of *phase transitions*, i.e., when a substance changes from one state to another.

The following are the basic conditions under which the formation of crystalline substance takes place:

(1) a change from the liquid phase to the solid—crystallization occurs from a melt or a solution;

(2) a change from the gaseous phase to the solid—crystallization occurs by sublimation;

(3) a change from one solid phase to another, accompanied by alteration of the shape of the crystal structure; this phenomenon is called *recrystallization*; it should not be confused with repeated crystallization, when mother liquor is poured off each time and the crystals are dissolved in a fresh portion of solvent.

The three cases of formation of crystalline matter are not equally widespread; the first case is observed much more frequently than the second or the third.

1. Crystallization from a melt or a solution often occurs on a very wide scale both under natural conditions and in industry, as e.g. the formation of massive crystalline rocks during solidification of a magma, deposition of thick salt beds at the bottom of salt lakes and periodically drying bays, solidification of molten metals, manufacture of various products at chemical plants, etc.

Deep-seated massive crystalline rocks are formed in three stages of crystallization: primary, principal, and residual.

During the *primary stage*, when the melt is still very hot, individual crystals are formed of those chemical compounds, i.e., minerals, which have the highest melting point. The crystals can grow freely developing their particular forms. Such freely developed crystals are called *idiomorphic*.

As the melt cools, the number of substances crystallizing from the magma progressively increases, and the process of crystallization becomes more intense. The second, *principal stage of crystallization*

begins. Individual crystals cannot develop freely because their growth is hindered by adjacent crystals of the same or other minerals: a struggle develops for free ions and space. The boundaries of individual crystals often depend on the shape of the neighbouring or earlier formed crystals which prevent the free growth of later crystals.

During the last, *residual stage* the change from the liquid to the solid phase is forced by a considerable drop of temperature. Stray ions fill the remaining vacant places, sometimes forming glass, i.e., amorphous, not crystalline, substances.

When magma solidifies at or near the surface, cooling proceeds much more rapidly, and the whole process is considerably speeded up. In this case a larger quantity of material crystallizes during the last stage, thus forming volcanic glass.

2. During sublimation crystals are formed directly from vapour, by-passing the liquid phase. The specific feature of the crystals thus formed is usually their small size and sometimes skeletal form.

Sublimation occurs naturally in so-called *dry fissures*, on the walls of which various minerals are deposited on cooling of the rising gases. We can often observe this process in winter, when hoar-frost and various ice patterns are formed on window panes. Coloured haloes around the sun, and on frosty nights around the moon or some bright stars, are due to the refraction of rays in minute ice crystals formed in the atmosphere from water vapour.

In the chemical industry sublimation is used for separation and purification of many products (e.g., iodine, naphthalene, camphor). In laboratories the results of sublimation appear as white coatings on reagent jars and glass panes of exhaust cabinets. Sublimates of different colours on charcoal or in test tubes serve in analytical chemistry as identification features of some elements (arsenic, antimony, zinc, mercury, etc.).

3. The least studied process of the formation of crystals is recrystallization in the solid state. It consists of enlarging of tiny crystals of various aggregates under the action of deformation forces, periodic stresses, and temperature variations. For instance, pressure sometimes causes chalk (submicroscopic crystals of calcium carbonate) to change into distinctly crystalline marble. Fine-grained iron of some parts of machinery becomes coarse-grained as a result of constant jolting and directed impacts. The process of recrystallization can be used for obtaining large single crystals of metal.

What is the initial stage of crystallization like? We know that in gases and liquids the molecules are perpetually in motion and that in gases molecules move much more rapidly than in liquids. If we accept the theory of intermolecular forces of attraction and repulsion, we can picture molecules graphically as dipoles with

positive and negative charges concentrated at definite points (Fig. 9). As the temperature falls, the speed of molecular movement is reduced. With the transition to the solid phase the particles may be either arranged at random with respect to each other or may be mutually oriented. In the first instance we shall have an amorphous solid phase which can be regarded as a supercooled liquid. In the second instance the positive and negative regions of the molecules may become the primary nuclei of a crystal lattice upon assuming a stable position (see Fig. 9).

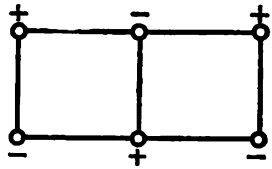


Fig. 9. Arrangement of molecules in nuclei

A nucleus is a microscopically minute crystal which is in a state of complete equilibrium with a supersaturated solution.

A strongly supersaturated (labile, i.e., unstable) solution in which crystallization has started appears to be a mass of randomly moving particles (molecules, ions) and crystal nuclei (submicrons). The nuclei may be unidimensional, two-dimensional, and three-dimensional tiny crystals of different shapes and sizes. Some nuclei grow, others dissolve, but on the whole growth is predominant. Nucleus growth results either from adherence of individual molecules to a crystal, or from cohesion of nuclei, mainly two-dimensional ones or lamellate three-dimensional nuclei formed from two-dimensional ones. During their growth crystals tend to assume an equilibrium form; but ways of attaining an equilibrium form are not always the shortest possible, therefore initial crystal forms (still in the process of growth) differ considerably from forms which have attained equilibrium. If the total excess of substance in a supersaturated solution has crystallized before the crystals have assumed an equilibrium form, continued change in this form can proceed only at a very slow pace. Therefore, practically all crystals, irrespective of their form, will have attained equilibrium with the saturated solution. A slightly supersaturated (metastable) solution has no crystal ultramicrons, and crystal growth in it is possible only on introduction of nuclei from outside.

All liquids are capable of becoming supercooled to a greater or lesser extent. For instance, glycerine and melted salol can be cooled to a temperature much below their crystallization point without transition to the solid state.

When supercooling occurs, the curve of Fig. 8 assumes a different appearance (Fig. 10). It was obtained for a substance normally crystallizing at 23° C. Supercooling was carried down to 9° C (23°—9°=14° C). Crystallization thus started at +14°, but the exothermal reaction raised the temperature to +23°. In cases of considerable supercooling (dotted part of the curve) the temperature may not even rise to the normal level.

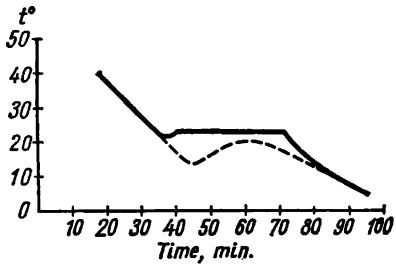


Fig. 10. Cooling curve for a substance crystallizing from a supercooled solution

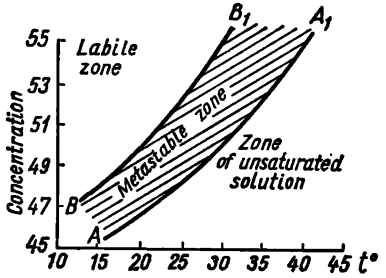


Fig. 11. Three zones in a solution

Viscous liquids, in which the molecules move much more slowly than in labile liquids, often solidify without crystallization on sufficiently rapid cooling, i. e., they acquire an amorphous structure.

In the majority of cases the nucleation and growth of crystals occur at a lowering in temperature of the melt and the accompanying supersaturation of the solution. Initial crystallization may be artificially induced (by introducing a seed crystal) or spontaneous. Tiny crystals of the crystallizing substance itself are the best seeds, although dust particles with a structure closely resembling that of the crystallizing substance often prove suitable enough. Supersaturated solutions from which all nuclei have been carefully removed during their preparation can be kept in hermetically sealed vessels for long periods of time without crystallization. Supersaturation has certain limits, however, beyond which spontaneous crystallization is inevitable.

The process which takes place in such a case can be explained as follows. Above the solubility curve AA_1 (Fig. 11) there is another curve BB_1 which is called a *supersaturation curve*. To the right of the AA_1 curve is the zone of unsaturated solutions. To the left of the BB_1 curve is the zone of *labile solutions* in which crystallization begins spontaneously. Between the two curves is located the *metastable* zone*; the ratio of concentration and temperature for

* The word metastable is of Greek origin and means nearly stable.

forced crystallization is dependent on the boundaries of this zone.

Changes in crystals with time occur mainly on their surface. Crystal growth results from the deposition of the compound of which it is composed on its surface, therefore it may be said that every particle of a crystal formed was at some time a part of that surface. Hence the shape of a crystal is its present, while the internal structure (and texture) is its past.

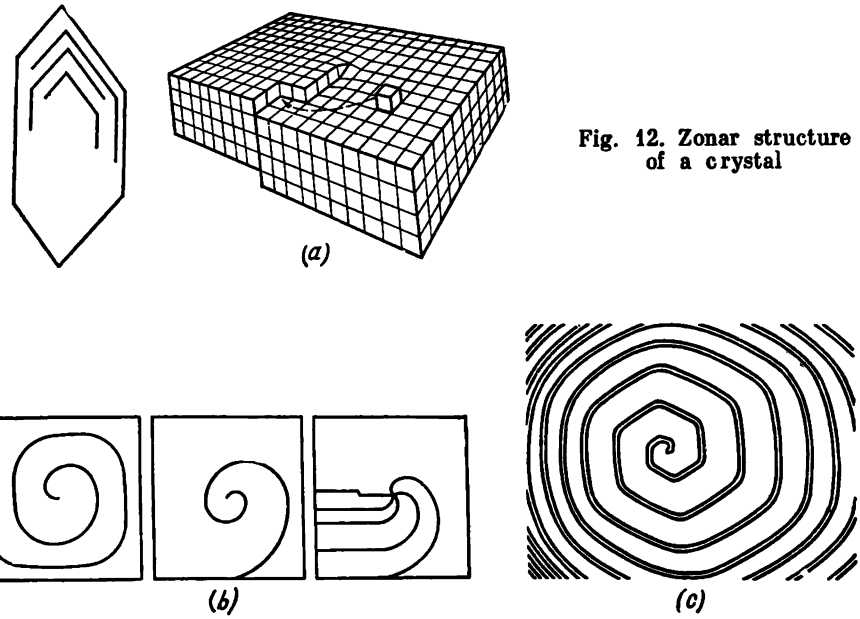


Fig. 12. Zonar structure of a crystal

A natural crystal, as a mineralogical phenomenon, is a heterogeneous entity consisting of closely interconnected parts.

The principal laws of crystal growth can be established through a study of sections of natural or artificial crystals. If in the course of growth some factor affecting the homogeneity or chemical composition of the crystal should vary, the latter will acquire a so-called *zonar structure* (Fig. 12), which frequently occurs in minerals and can be observed sometimes in smoky quartz, where weak and strong colouring alternate in layers, or in crystals of fluorite (CaF_2), where colourless layers often alternate with those tinted bright violet or green.

Examination of crystals with a zonar structure will show that *during growth the faces of a crystal are translated parallel to them-*

selves. The measurement of the thickness of different layers in crystals with a zonar structure shows that different faces grow at different rates (by the rate of growth is meant the increase in thickness per unit time). The growth of a crystal face does not occur as a deposition of plane layers, for new material particles are deposited in a spiral (Fig. 12, *a*, *b*). Traces of such deposition can be observed on the faces of crystals which have ceased growing, i.e., which have been removed from the solution (Fig. 12, *c*).

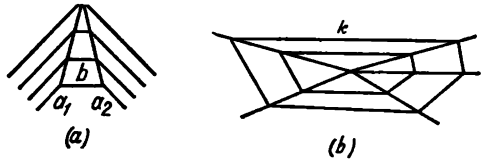


Fig. 13. Growth of faces:
(*a*) face *b* tapers out; (*b*) face *k* does not taper out

Knowing the shape and the dimensions of a crystal at a particular moment, as well as the rate of growth of its faces, we can predict what its shape will be at any point in the future (taking the rate of growth to be constant). To do this it will suffice to draw lines normal to the crystal faces and proportional to the rate of growth, and to draw planes perpendicular to these lines until the planes intersect. The relative dimensions of faces will alter in this process: some faces will grow larger, and others smaller. In the majority of cases those faces will increase which have the lowest rate of growth; the rapidly growing faces gradually become smaller and may finally disappear completely. This rule holds true only under particular geometrical conditions. Fig. 13 shows two cases of crystal growth. In the first case (Fig. 13, *a*) faces a_1 and a_2 grow slowly, while face *b* grows rapidly; it is obvious that the latter will gradually taper out and eventually disappear. In the second case (Fig. 13, *b*) face *k* will never disappear, no matter how high the rate of its growth may be.

When a crystal grows perfectly uniformly, its coigns progress along straight lines, the edges progress along planes, while the loci of faces form pyramids of growth. All these loci converge to a single point—the initial nucleus of crystallization (Fig. 14). Actually such an orderly arrangement of pyramids of growth is exceptionally rare. Usually the loci of development are broken and curved because of non-uniform growth. Crystals are never perfectly uniform. It can hardly be imagined that the solute could be deposited from a solution on a growing face in a perfectly plane layer. It is much

more probable that this deposition will occur through adhesion of molecular aggregates to a face, the aggregates inevitably differing from each other in size, though ever so slightly. Let us imagine an ideal face. When the first layer is being deposited, the molecular aggregates are arranged parallel to each other, but with free space between them. In the next layers incomplete parallelism begins to tell, as a result of the varying thickness of the aggregates deposited earlier. As the latter decrease in size, the structure of the crystal will approach the ideal pattern. In a considerably supersaturated solution crystals grow almost exclusively as a result of adhesion of spontaneously developing nuclei. The molecular aggregates are naturally large, and the spaces between them are filled with mother liquor and foreign matter. The resulting crystal is turbid and has low mechanical strength. In a slightly supersaturated solution conditions are more favourable for obtaining crystals of nearly ideal structure, but here too the degree of uniformity is inversely proportional to the rate of growth.

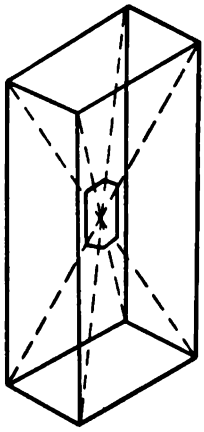


Fig. 14. Pyramids of growth

The following factors have the greatest effect on the shape of the growing crystal.

1. Concentration Currents. The portions of a supersaturated solution directly adjoining a crystal give up their excess of solute to the crystal. As the concentration of these portions of the solution thus decreases, the solution becomes lighter and rises up. Its place is taken by heavier portions, and the cycle is repeated. As a result, a zone of weaker concentration is built up above the growing crystal. The currents that develop in the process are called *concentration* currents. The larger the growing crystal, the stronger are the currents (Fig. 15).

If the crystal lies at the bottom of a vessel, its side faces have the most favourable conditions for growth. The lower parts of the faces are surrounded with more supersaturated solution than are the upper parts, this resulting sometimes in the appearance of steps and furrows on the lower portions. The faces inclined at obtuse angles to the bottom of the vessel grow more rapidly than those forming acute angles. The top face, which is the slowest growing one, is often very well formed (i.e., it is plane and smooth), if there have been no interfering eddies. The bottom face either does not grow at all, or grows only along the edges because of supersaturation diffusion; in this case a stepped indentation is formed in the face (see Fig. 15).

If the crystal is suspended in the solution, its bottom face is the one best supplied, and grows more rapidly than the other faces, and the crystal becomes elongated downwards.

Thus, the concentration currents strongly influence the shape of the growing crystal: if it is at the bottom of a vessel, the currents tend to make it flat; if it is suspended, they tend to elongate it.

The effect of the concentration currents can be eliminated by rotating the crystal about a horizontal axis or by shaking the crystallizer.

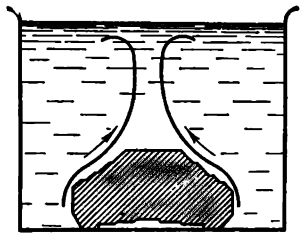


Fig. 15. Concentration currents

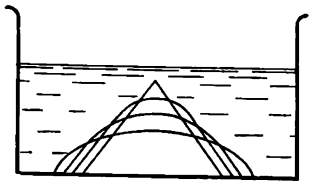


Fig. 16. Effect of alternate increase and decrease of temperature on a crystal growing in solution

2. Temperature Variations. This factor determines to a large extent the solubility of most substances and the shape of a growing crystal.

Let us imagine a crystal in a saturated solution at the bottom of a flat vessel (Fig. 16). When the temperature rises, the solution becomes unsaturated and the crystal begins to dissolve. The more concentrated solution thus formed flows down, preventing the lower part of the crystal from dissolving any further and facilitating the dissolution of its upper part. The solution becomes laminary in the process. When the temperature is lowered, the crystal grows mainly in its lower part, as the solution there is more concentrated, while the concentration currents cause the displacement of the solution. This cycle is repeated at each rise and drop in temperature. The crystal becomes flatter and flatter until it is a plate of zonar structure occupying the whole bottom of the vessel. A crystal suspended by a thread will under these conditions soon drop to the bottom, as its top part, which the thread is affixed to, dissolves. If two crystals are placed one above the other, the lower crystal will grow at the expense of the upper.

It should be noted that temperature variations often cause faces to appear which would never be formed under normal conditions of growth.

3. Degree of Supersaturation of Solution. This factor affects the homogeneity of crystals, which are less homogeneous when formed in strongly supersaturated solutions, and more homogeneous in slightly supersaturated solutions. The degree of supersaturation has, moreover, a considerable effect on the shape and the number of crystal faces.

4. Impurities in the Solution. Impurities often strongly affect the crystal shape. A classical example is the introduction of carbamide into a solution of sodium chloride. Without this addition sodium chloride crystallizes in cubes, with it—in octahedra.

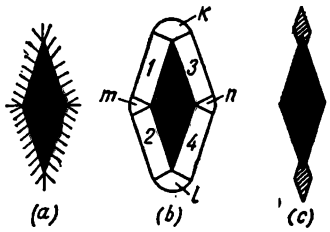


Fig. 17. Development of skeletal forms in crystallization from a viscous solution

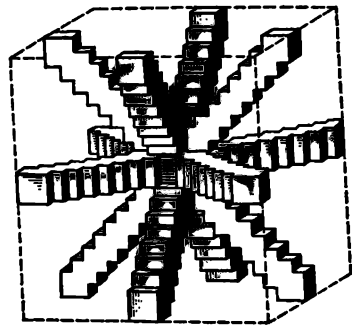


Fig. 18. Skeletal form of a crystal of metallic copper

5. Viscosity of the Solution. If the viscosity is high enough, it will prevent the formation of concentration currents. Then the crystal will be able to grow only through diffusion of supersaturation, which has a peculiar effect on the shape of the growing crystal.

To understand what goes on in this case, let us imagine that the crystal has only one infinitely large face. The supply of solute must come along lines which are normal to this face and which we shall call *lines of diffusion current*. These lines are uniformly spaced throughout the face. Actually the lines will be curved near the coigns and edges of the crystal (Fig. 17, *a*) as the faces are supplied from portions *1*, *2*, *3*, and *4* (Fig. 17, *b*), while the edges and coigns have additional feeding portions *k*, *l*, *m*, and *n*. Therefore, the crystal grows more intensely in the *k*, *l*, *m*, *n* portions where correspondingly thicker parts appear (Fig. 17, *c*). These thicker parts unbalance still further the distribution of feed to the individual parts of the crystal, and therefore it grows mainly in coigns, developing so-called *skeletal forms* (Fig. 18). These forms can also develop in a strongly labile liquid which for one reason or another is not stirred. Sometimes skeletal forms develop on sublimation.

EQUILIBRIUM FORM OF CRYSTALS

Formation of an interface at constant temperature, pressure, and quantity of substances making up the phases involves some expenditure of energy. The work done in forming a unit interface is called *surface tension* and designated by σ.

As the rates of growth of different faces of the same crystal are different, the faces have different surface tension.

The *equilibrium crystal form* is a form which at a given volume of the crystal corresponds to the minimum surface energy expended in its formation. This form should satisfy the following two requirements:

$$E = \sigma_1 s_1 + \sigma_2 s_2 + \ldots = \min,$$
$$V = \text{const.},$$

where s_1, s_2 = areas of faces with surface tension σ_1, σ_2 ...
E = total surface energy of a polyhedron
V = volume of a polyhedron.

Gibbs (1878) put forward the theory that a crystal tends to assume an equilibrium form during growth. To acquire the most stable form, the one we call an equilibrium form, a crystal must be repeatedly thrown off balance by the introduction into it of small amounts of energy in the form of heat. Thus, the crystal will have an opportunity of returning during subsequent cooling that quantity of energy which it can release under given conditions. It has been shown experimentally that a ball made from an alum crystal and placed in a saturated solution becomes an octahedron of the same weight in the course of several months under influence of temperature variations (i.e., as a result of repeated growth and dissolution). This octahedron is obviously the equilibrium form of an alum crystal in a saturated aqueous solution.

It is evident from the above that crystal forms—both natural and artificial—usually encountered in practice, are not equilibrium forms at all.

We may visualize three types of crystalline formation: *unidimensional*, *two-dimensional*, and *three-dimensional*. In formations of the first type (molecule, atom, ion, a group of atoms) crystal particles form chains, in formations of the second type—polygonal layers, and in formations of the third type—polyhedra.

RELEASE OF ENERGY IN CRYSTALLIZATION

We have already seen that crystallization is accompanied by a release of energy, usually in the form of heat. If the quantity of energy released in forming a unit weight of each of the three types

of crystalline formation be designated as e_1, e_2, e_3, respectively, we shall have the relation $e_1 < e_2 < e_3$, since there are more unutilized bonds on a crystal surface in unidimensional and two-dimensional formations, than in three-dimensional ones.

The above is true of large crystals. In very small crystals the quantity of heat released greatly depends on the position of each individual particle. For instance, if a particle adheres to a crystal with one of its faces, the quantity of heat released will be smaller than if the particle adheres to the crystal with two or three faces. There is no direct relationship, however, between the quantity of heat

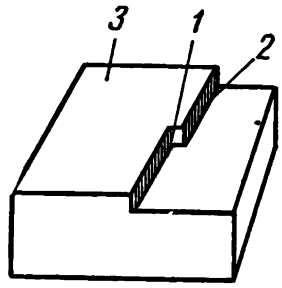


Fig. 19. Three cases of implanting a particle during growth

released and the number of adhering faces, because the place at which the particle adheres—in the middle of a face, at the edge, or at the coign of a polyhedron—is also important. Theoretically cases are possible in which less energy is released in the formation of very small three-dimensional crystals consisting of a few molecules, than in the continued growth of a large two-dimensional crystal.

In the course of slow, undisturbed growth particles are deposited on a crystal mainly in a manner producing the greatest release of energy.

If a crystal is at the stage of growth shown in Fig. 19, the greatest quantity of energy will be released when a particle adheres to a three-faced corner (*1*), a smaller quantity, when it settles in a two-faced corner (*2*), and still smaller, when it settles on a face (*3*). This explains why a second layer cannot be formed on a face until the formation of the first layer has been completed. This does not mean that the second layer cannot begin developing before the first one is completed; it can begin growing, but the conditions will not favour it. Therefore, in the case of a two-dimensional crystal its growth is more easily continued in the form of a plate than by transformation into a three-dimensional crystal through the addition of a second layer.

CHARACTERISTIC FEATURES OF THE DISSOLUTION OF CRYSTALS

A crystal placed in a pure solvent or in an unsaturated solution begins to dissolve. The coigns and edges dissolve quicker than the faces, and the crystal becomes somewhat fused in form. This is explained by the fact that the particles released when the outermost portions of faces are dissolving have greater freedom of movement than those from the centre, they break away more easily from the crystal, and provide access for the solvent to the underlying layers.

Observations have shown that the process of dissolving is characterized by the following phenomena.

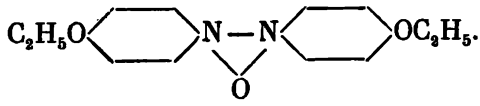
1. While during crystal growth the most stable faces are the slowly growing ones, in dissolution those faces appear on a crystal that dissolve the fastest.

2. The rate of dissolution is a continuous function of the direction of growth of the crystal face.

3. In the course of dissolution microscopic multifaceted pits are always formed on crystal faces—these are the so-called *etch figures* or, in other words, *dissolution figures*, which are of considerable morphological significance. They are most easily obtained through the action of a weak solvent, and will either cover the face completely, making it appear dull, or they will form at only a few points. In the latter case the etch figures are usually fairly large and distinct. The opposite phenomena—*mounds of growth* appear much more rarely and are of an entirely different origin, since they are produced not only by growth, but also by periodic growth-dissolution cycles.

4. The most perfect surfaces are developed on those faces of a growing crystal which have the slowest growth rate. The surfaces with the slowest dissolution rate always appear dull.

Crystals of some organic substances, when heated, turn into liquids that have the optical properties of uniaxial crystals (see Ch. XV). Such formations are called liquid crystals or crystalline liquids. About 250 such formations are known at present. Most of them are organic compounds of the aromatic series. They consist of molecules of a greatly elongated form. For instance, paraazoxyphenetol has the structure



A liquid crystalline substance is formed as a turbid liquid consisting of drops of homogeneous liquid crystals oriented in different directions. A good example of this is sodium oleate (soap). Structurally, liquid crystals can neither be classed with amorphous nor with crystalline substances.

PRACTICAL METHODS OF OBTAINING SINGLE CRYSTALS FROM A MELT

Growing large individual crystals from a melt in the form of natural polyhedra is a difficult task, and therefore experiments are usually limited to obtaining single crystal blocks.

Three methods of growing single crystals from a melt are generally used: (1) the Kyropoulos method; (2) the Bridgman method (with a drawn-out tube); (3) the Verneuil method.

All these methods are based on the phenomenon of selection. If, for instance, a number of small crystals start developing at the same time at the bottom of a vessel, in the course of further growth their number will decrease, and finally only one crystal will "survive" and keep on growing. The reason for the selection is concealed in the geometry of crystal growth and in the initial orientation of crystals.

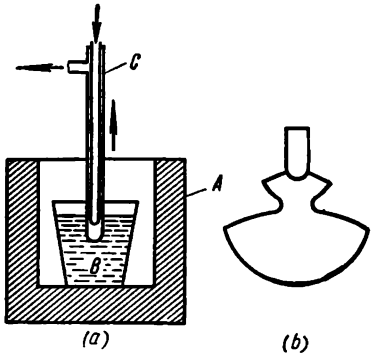


Fig. 20. Kyropoulos device

1. The *Kyropoulos device* (1926) consists of an electric resistance heater *A*, a platinum crucible *B* and a cooler *C* (Fig. 20, *a*). The cooler is a platinum test tube through which air can be blown by means of an inner copper tube. The cooler can be lowered mechanically into the crucible and very slowly withdrawn from it.

When the substance selected for crystallization has been melted in the crucible and considerably superheated, the cooler is lowered into the melt and air is blown through it. Blowing is increased and the cooler is slowly lifted when a hemispherical growth of fine crystals has formed at its tip (Fig. 20, *b*). When the hemisphere comes into contact with the surface of the melt, only one of its numerous crystals usually survives and continues growing as the cooler is lifted higher.

This is an efficient method for growing fairly large crystals of sylvine (KCl) and of many other salts and pure metals.

2. Single crystals of fusible metals are obtained by the *Bridgman method* (1925). A heat-resistant glass or quartz tube with the bottom end drawn out into a capillary is filled with a melt and suspended vertically in an electric tube furnace (Fig. 21). The metal is cooled by gradual lowering of the glass tube into another tube, of lower temperature. Crystallization begins in the capillary where the

selection phenomenon takes place. Eventually the whole tube is filled by a single metal crystal.

The Bridgman method is excellent for obtaining single crystals of zinc (melting point 419° C).

3. For heat-resistant substances, e.g., for corundum (Al_2O_3), the *Verneuil method* (1934) is used.

The substance to be crystallized is placed in the form of a very fine powder into a vessel *L* with a wire net bottom (Fig. 22). When

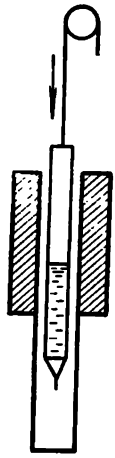


Fig. 21. Bridgman device

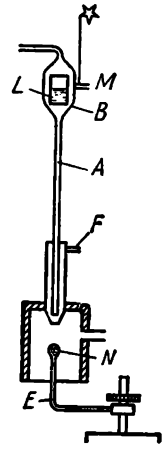


Fig. 22. Verneuil device

a hammer *M* periodically strikes the wall of a container *B*, the powder spills along a tube *A* into the flame of a hydrogen burner *E* made of a refractory material where it is sintered into a friable mass; the oxygen supply comes also down the tube *A* and mixes with hydrogen coming in at *F*. As the cone *N* of the sintered mass attains a certain size and form, the conditions of combustion of the gas change, as a result of which the apex of the cone becomes somewhat fused thus giving birth to a nucleus. After that the temperature of the flame at the cone apex is so adjusted that the melted particles of powder fall on the nucleus which, steadily growing upwards, produces a single crystal droplet.

Here, as in other instances of single crystal growing described previously, only one of the many initially formed crystals survives.

S. K. Popov (Institute for Crystallography of the Academy of Sciences of the USSR) has designed a device for producing thin single-crystal rods of cylindrical shape. This is of great practical importance, as crystals of red corundum are widely used in the

watch-making industry as "stones". Insofar as these stones are of cylindrical shape, they can be easily obtained by sawing the rod across.

CRYSTALLIZATION FROM SOLUTION

Crystallization from solution consists in the giving off of excess solute by the solvent. Hence crystals can be formed only from supersaturated solutions.

The *coefficient of solubility* may be defined as that weight of substance which will dissolve in 100 g of solvent.

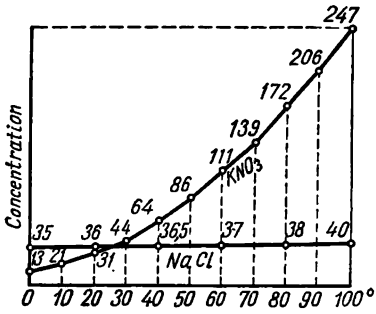


Fig. 23. Solubility curves for KNO_3 and NaCl

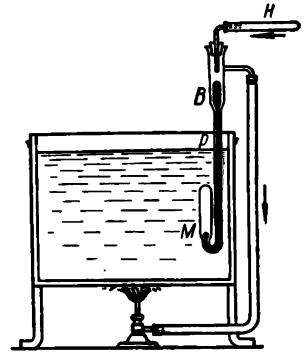


Fig. 24. Wulff thermostat

Supersaturation can be brought about in two ways: (1) by removal (evaporation) of the solvent; (2) by lowering the temperature, as this will result in a decrease of solubility for most substances.

The shape of the solubility curve will show which of the two methods should best be used in a given case.

Two types of solubility curves may be singled out (Fig. 23). In one case (KNO_3) an increase in the temperature of the solution results in a very sharp increase in solubility. In the case of NaCl, however, an increase in temperature from 0° C to 100° C results only in a very small increase in solubility—the quantity of substance which can be dissolved increases by only 5 g. Hence, to obtain some nitre crystals quickly it is necessary to dissolve the substance in boiling water and then to cool the solution. But this method is obviously impractical in the case of sodium chloride; to obtain its crystals the solution should be vigorously evaporated.

In the great majority of cases temperature variations strongly affect the solubility of substances, therefore crystallization has to be conducted in thermostats—devices with automatic temperature control. There are a number of thermostats of different types. Air

is the medium of temperature control in some, while in others it is water. Crystallization is mostly conducted in water thermostats. They were devised by G. V. Wulff and perfected by his pupil A. V. Shubnikov. Heating can be done by electricity or gas.

The gas-heated water thermostat designed by G. V. Wulff (Fig. 24) consists of a metal tank several tens of litres in capacity, with thermally insulated walls. It is heated from below by one or more gas burners with chamotte fish-tail nozzles to prevent back-firing when the flow of gas decreases considerably.

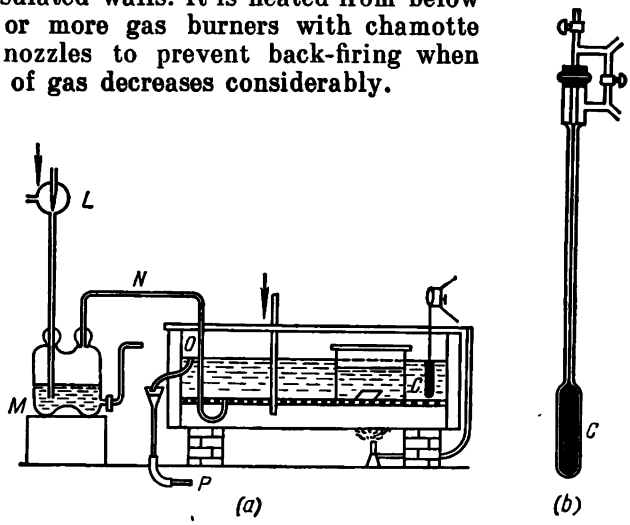


Fig. 25. Shubnikov thermostat:
(*a*) general view of a thermostat; (*b*) thermoregulator

On the way from the mains to the burner the gas passes through a thermoregulator, which is designed as follows. The reservoir *M* (Fig. 24) is filled with a liquid which has a high coefficient of expansion, and therefore the section *M* becomes very sensitive to temperature variations. In Wulff's thermostats the reservoir *M* of the thermoregulator is filled with toluene. A tube *p* is filled with mercury, the excess of which overflows into the reservoir *B*. Gas flows along the tube *H* and passes to the burner via the tube (see arrows in Fig. 24). As temperature rises, the toluene expands, and the level of the mercury in the reservoir *B* rises, thus limiting the space through which the gas passes, whereupon the burner gives less heat, the mercury drops, and the flow of gas to the burner increases. In the upper part of the reservoir *B* there is a small opening which the mercury cannot reach. This opening serves for letting through some gas to the burner when the mercury has closed the mouth of the tube *H*, so that the flame might not go out. Inside the thermostat there is a special device (not shown in Fig. 24) for continuous agitation

of the water in the vessel. Crystallizers are placed on special supports so that they are largely submerged. The water level must of course be below the walls of the crystallizers. Shubnikov has perfected Wulff's scheme in the following manner. Instead of a mechanical agitator he has introduced a pneumatic one (*LMN* in Fig. 25, *a*). A device *OP* has been added to maintain a constant level of water in the thermostat. The thermoregulator *C* has been made more convenient to use, and toluene has been replaced with mercury, since toluene vapours, penetrating between the mercury and the tube walls, attack the connecting rubber tubes. The Shubnikov thermostat has a capacity of about 1,000 litres. If well made, it will control temperature to within 0.01° C.

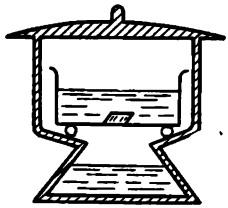


Fig. 26. Crystallization in a desiccator

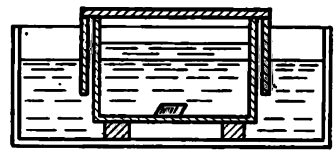


Fig. 27. Crystallization in a water thermostat

When crystals are grown by evaporation of a solvent, a crystallizer is placed in a hermetically sealed vessel containing a substance which absorbs the vapour of the solvent. Concentrated sulphuric acid is generally used in crystallization from aqueous solutions.

With small crystallizers it is convenient to use conventional desiccators (Fig. 26). The desiccator should be kept in a thermostat during crystallization, since even very small temperature variations cause defects in crystals. When the temperature rises, coigns and edges become fused, and at a subsequent drop in temperature vigorous growth begins in these spots, since the crystal tends in the first place to restore its multi-faceted form. Too rapid a growth results in the inclusion of small bubbles of solution, and often turbid portions appear in the crystal.

Some slightly heated saturated solution is poured into a crystallizer and a tiny crystal seed is introduced. These operations should be conducted in as sterile conditions as possible, to preclude contamination of the solution by dust-size particles of the crystallized substance.

Growing of crystals from solution by lowering the temperature is carried out in the following way:

(1) a solution is prepared, which is saturated for the temperature at which crystallization is to be conducted;

(2) a weighed quantity of a substance is introduced into the solution and is dissolved by heating;

(3) a nucleus is introduced into the solution, and the crystallizer is left to stand in a thermostat.

The dissolved excess of the substance should obviously precipitate in the form of crystals. Every substance has its optimum supersaturation value which is determined experimentally. For alum crystallized at room temperature it is 2-3 per cent by weight.

When large crystals are to be grown, an excess of the compound is dissolved, and the solution is filtered without any precautions against contamination by nuclei. The solution is left to stand for 2 or 3 days, and is frequently agitated during that period. A large number of crystals should precipitate, and the solution above them can be considered saturated. This solution is poured off into another flask where a weighed amount of dry compound is added, dissolved by heating, and the solution is filtered. The weight of the compound added should correspond to the weight of the future crystals. Hence it is possible to determine the volume of solution necessary for growing crystals of definite weight. A small well-formed crystal is placed in a still warm solution, the crystallizer is placed in a thermostat and sealed hydraulically (Fig. 27) to prevent contamination by nuclei from the atmosphere. If sufficient sterility has been observed, a single crystal of pre-calculated weight will grow in the vessel in 10-15 days.

CHAPTER III

Measuring of Crystals, and the Law of Constancy of Angle

It was mentioned in the first chapter that we visualize a crystal as a solid substance of reticular structure (Fig. 28). The particles of which it is made up constitute a crystal lattice, where faces correspond to planes, edges to rows of nodes, and coigns to nodes.

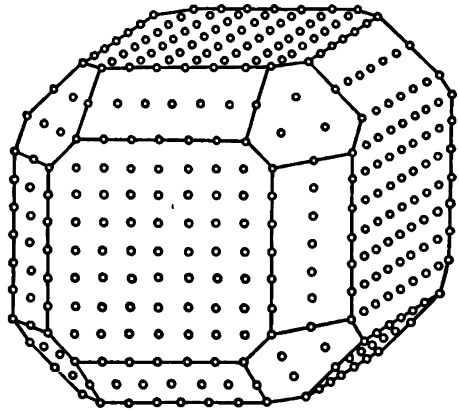


Fig. 28. Structure of a crystal

This should not be understood literally. If a microscope could be designed to show us directly the atoms and molecules, we should see that the structure of a real crystal is very much unlike that of a geometrically correct *space* lattice.

We shall discuss this later, in more detail, but for the present we shall adopt as a general scheme a lattice affording easy understanding and explanation of specific properties of crystalline substance.

Insofar as three nodes from different rows determine the position of each plane of a lattice, or of a plane net, as it is conventionally

called, it is evident that every lattice must have an infinite number of possible planes definitely positioned in space. Some planes are thickly covered with nodes, others not so thickly. Therefore, we can distinguish plane nets by *their degree of density*, i.e., *by the number of nodes per unit surface area* (*reticular density*).

If all the possible planes of a crystal lattice (their number being infinitely large) found reflection in the faceting of a crystal it would be difficult to find simple laws governing the faceting. On the other hand, it might seem that several crystals of the same chemical compound, i.e., crystals built according to the same lattice, might have entirely different habits and would have no two identical interfacial angles.

Actually the picture is quite different.

The crystals do not develop all the possible faces, but just a few of them. What faces are these and why? The following *law of consecutive development of crystal faces* can be formulated: habit faces, i.e., those appearing most frequently, are developed *in the order of decreasing densities of their nets*. Thus, the first faces appearing on a crystal have the maximum density, the ones appearing later have progressively decreasing densities. This can be roughly explained by the higher mechanical strength of faces with maximum densities and by their slower growth. Different substances display some very peculiar features in this respect. For instance, NaCl crystals have very few different faces (only 3 or 4 types); while other minerals, such as calcite, are richly faceted, the faces having nets of highly diverse densities.

Thus a crystal retains mostly those faces *which correspond to lattice planes of the highest reticular density*.

The small number of faces and their frequent, sometimes even constant, presence on a crystal, as well as their ability to be translated parallel to themselves during crystal growth, has served as a basis for the first fundamental law of crystallography—*the law of constancy of angle*: *crystals of the same substance can have different habits depending on the number and size of faces, but the angles between the corresponding faces remain constant.*

The law of constancy of angle was first formulated by the Danish scientist Nicolaus Steno (Nicholas Stensen) in 1669.

Since at the time scientific works were usually written and published in Latin, Stensen latinized his name. His work was called *De solido inter solidum naturaliter contento* (On a solid naturally contained in a solid).

The first edition was printed in Florence in 1669, the second ten years later in Leiden.

The constancy of interfacial angles was demonstrated by Stensen for two substances: quartz (SiO_2) and hematite (Fe_2O_3).

The validity of the law of constancy of angle for crystals of all substances was confirmed by the French scientist Romé Delisle much later, in 1783.

It should only be added that the constancy of angles takes place under identical temperature and pressure conditions.

It can be seen from the above that the angles of crystals, or the mutual inclination of crystal faces, are highly important. It is natural, therefore, that one of the first problems in the study of the external form of a crystal is the measurement of its interfacial angles.

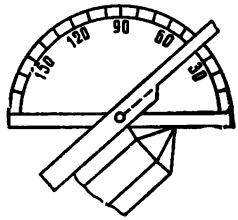


Fig. 29. Contact goniometer

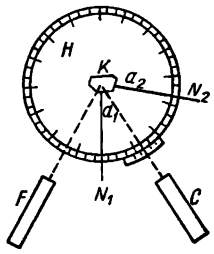


Fig. 30. Function of the reflecting goniometer

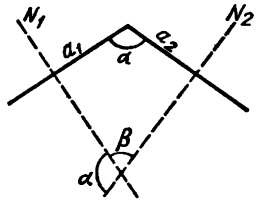


Fig. 31. Relationship between the interfacial angle and the angles between normals

This is accomplished with the aid of devices called *goniometers*. Different types of goniometers are used depending on the size of the crystal, as well as on the number and quality of its faces. The most widely used instruments are.

1. **Contact goniometer** consists of a protractor and a rotating bar pivoted about the centre of the protractor (Fig. 29). In the measurement of an interfacial angle the goniometer is applied to the crystal so that the edge between faces is parallel to the axis of rotation of the bar. Such instruments are accurate to within 30′, and are used when a more accurate measurement is impossible, usually because of the size of the crystal or of the imperfection of its faces.

The first contact goniometer was built by Carangeot in 1782. At the present time measurements of large crystals are made with improved instruments of this type.

2. **One-circle reflecting goniometer** is designed on the principle of obtaining consecutive reflections of rays of light from crystal faces. It is shown diagrammatically in Fig. 30. A crystal *K* is mounted with the aid of wax on a holder connected to a stage which rotates together with a graduated circle *H*. The edge between the faces being measured is placed parallel to the axis of rotation. Rays

from a source of light pass through a collimator* C and strike the crystal in a parallel beam. The observer looking through a telescope F sees the image of the source of light, called a signal, only when one of the crystal faces (a_1) occupies the position shown in Fig. 30, i.e., is normal to the bisectrix of the angle between the optic axes of the collimator and the telescope.

Having taken a reading with the aid of a nonius, corresponding to the required position, and having rotated the crystal together with the graduated circle so that the face a_2 takes the place of the face a_1 (or lies parallel to it), we can find the angle between normals N_1 and N_2 by the difference in readings. This angle, β (Fig. 31), is complementary (to 180°) to angle α between the faces a_1 and a_2. A complete revolution of the crystal makes it possible to measure all the angles of one zone.

The one-circle goniometer allows measurements to be made with an accuracy of 1′ or higher. The first instrument of this type, invented in 1809 by W. H. Wollaston, had a vertical graduated circle. It had neither a telescope nor a collimator, and afforded a much lower accuracy of measurement. The principal drawback of the one-circle reflecting goniometer is the impossibility of measuring interfacial angles of more than one zone at one setting of a crystal. When a crystal 3-4 mm in size has a large number of faces (25-30), measurement by zones is complicated and labour-consuming. The crystal has to be reset several times, this involving repeated mounting. In each mounting the crystal has to be set up so that some faces from one or two previously measured zones might be included. This increases the difficulties in mounting.

Two-circle reflecting goniometer or a **theodolitic goniometer** has two mutually perpendicular axes of rotation (Fig. 32) and accordingly two graduated circles, a telescope, and a collimator. The position of a crystal corresponding to a signal in the telescope can be noted by taking readings off the two graduated circles. Thus, two spherical coordinates are obtained for each face, this allowing to determine its position in space.

The idea of a two-circle goniometer was first conceived by professor W. H. Miller (1801-1880) of Cambridge University. In 1874 he had to measure a platinum bead which was obtained in the flame of a blowpipe. The globular bead, only 0.73 mm in diameter, had 147 faces. Professor Miller combined a one-circle goniometer of the Babinet type with a small Wollaston goniometer so as to obtain mutually perpendicular axes of rotation. This goniometer is still at the mineralogical museum of the Cambridge University. 15 years

* A collimator is that part of an optical instrument which produces a beam of parallel rays.

later, in 1889, a genuine two-circle goniometer was built by Fedorov.

The Fedorov two-circle goniometer (Fig. 33) had no collimator, and an autocollimation device was installed in the telescope. But soon Fedorov himself saw the disadvantages of this arrangement and replaced the collimator with a source of light sufficiently removed from the instrument.

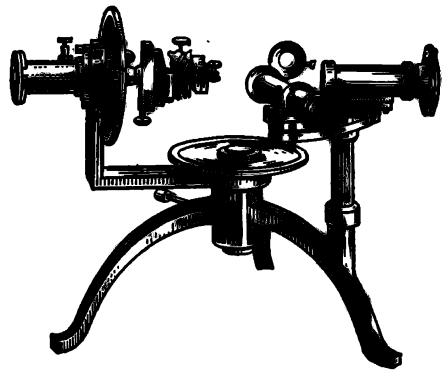


Fig. 32. Two-circle goniometer

Fedorov's work on the design of two-circle goniometers was carried on by E. E. Flint. In 1938-1939 he succeeded in organizing the manufacture of two-circle goniometers of his own design in the workshops of the Moscow Institute of Geological Prospecting. These instruments (Fig. 34) differ from other models in the ease of preliminary setting and its retention. Any reflecting goniometer, whether one-circle or two-circle, requires very careful preliminary setting and checking. In the one-circle goniometer the optic axes of the telescope and the collimator should lie in the same plane perpendicular to the axis of rotation. The telescope should be set at infinity, and the collimator should project a parallel beam of light upon the crystal. In two-circle models the horizontal axis of rotation, as well as the optic axes of the collimator and the telescope, should lie in the same plane perpendicular to the vertical axis, with all the four axes intersecting at the same point. Therefore the procedure of preliminary setting of a goniometer takes up very much time and labour and should be resorted to as rarely as possible. The goniometer should be so designed as to retain its initial setting and not become unsettled during crystal measurements. Flint's models are satisfactory in this respect.

Besides the instruments of Russian design, there are two-circle goniometers of Czapski and of Goldschmidt. Goldschmidt's

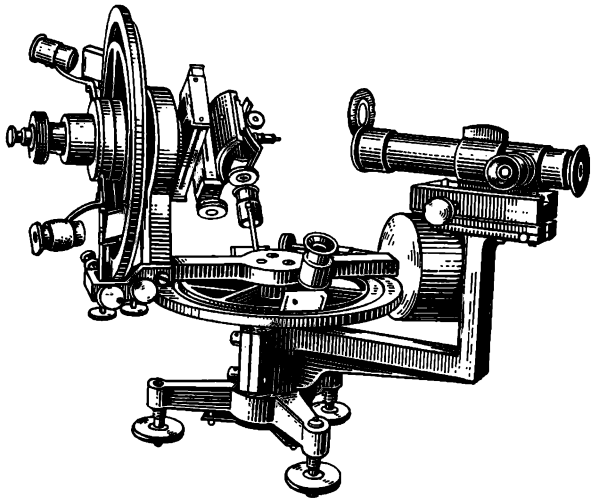


Fig. 33. Fedorov goniometer

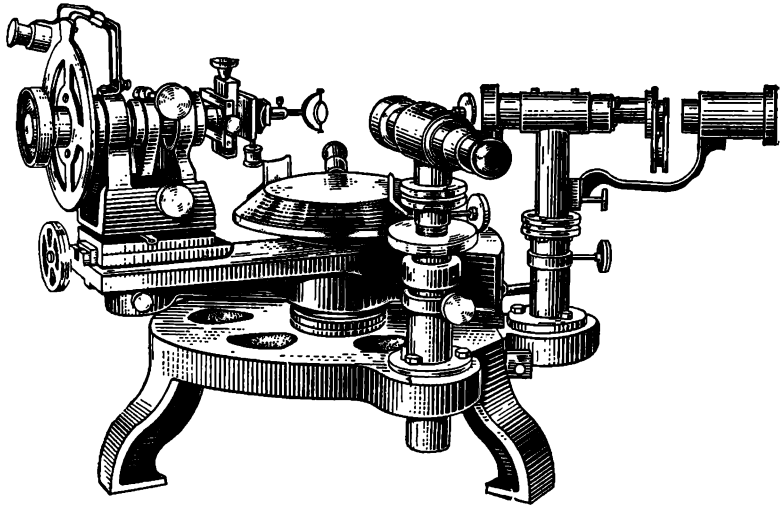


Fig. 34. Flint goniometer (model 1)

instruments have a very well-designed and convenient telescope.

The use of two-circle goniometers considerably simplified the procedure of crystal measurement. They were first introduced in 1893 and were soon accepted universally.

Besides the above-mentioned goniometers designed for measurements of medium-sized crystals (1 to 5-6 mm), there are instruments for measuring very large or very small crystals. There are also goniometers for special purposes, e.g., for measuring crystals at very high and very low temperatures, for making thin oriented sections, for measurements of crystals in a solution during growth.

TREATMENT OF THE RESULTS OF THE MEASUREMENT OF CRYSTAL ANGLE. CRYSTAL PROJECTIONS

One of the most important features of a crystal is the constancy of its interfacial angles, the faces themselves varying greatly in size and number. Therefore crystals should be represented in a way which would bring out this fundamental feature, i.e., would give a clear idea of the size and mutual arrangement of interfacial angles. The various methods of projection described below are used to provide such representation.

If normals are drawn from an arbitrary point in space to all faces of a crystal, we shall have a bundle of straight lines converging at the selected point. The angles between these lines will be complementary (to 180°) to the central angles between faces.

By describing a spherical surface from the point of intersection of the normals (Fig. 35) and extending the normals until they cut the surface, we shall obtain a number of dots on the sphere which show unequivocally the arrangement of the faces; this will be a *spherical projection of a crystal.* These dots are called *poles* of faces. Their positions on the sphere can be determined through their spherical coordinates—latitude and longitude—as is done in geography. But instead of the latitude which is read from 0° at the equator *EE* to +90° at the north pole and −90° at the south pole of the sphere, it is more convenient to use another coordinate—a so-called *polar distance* which is read along any meridian from 0° at the north pole to 180° at the south pole. With this method all points of the equator will have a polar distance of 90°.

The spherical coordinates used in crystallography have the following designations: ρ—polar distance, and φ—longitude. The latter is read along the equator from whatever meridian has been taken as initial. Fig. 36 shows ρ and φ for face *M*.

Several methods are used in changing from a sphere to a plane drawing. Most convenient for various graphical calculations and plotting are two methods: gnomonic and stereographic projections.

Gnomonic Projection. The plane of projection is placed tangent to the sphere, in the centre of which is the point of vision. The straight lines connecting this point with the face poles are extended until they intersect the tangential plane G on which the gnomonic projection of a crystal is obtained (Fig. 37).

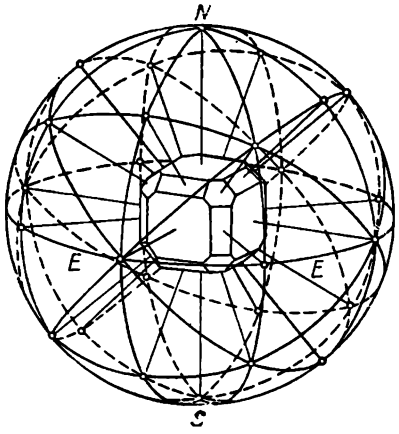


Fig. 35. Spherical projection of a crystal

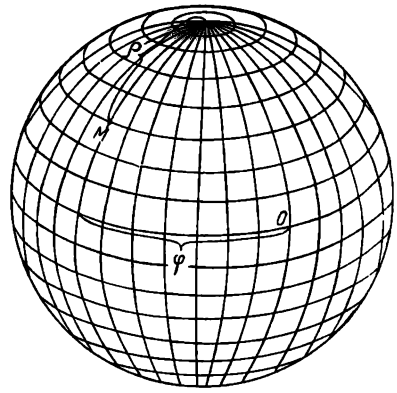


Fig. 36. ρ and φ coordinates on a sphere

Stereographic Projection. The plane of projection cuts the sphere diametrically, i.e., through the centre, and produces the primitive circle E of the projection (Fig. 38).

The point of vision is at one of the poles of this circle. Straight lines connecting the point of vision O with the face poles on the sphere across the plane of projection leave a corresponding number of dots on the plane, these dots constituting the stereographic projection of a crystal. Face poles that lie on the primitive circle, represent their own projections.

Stereographic projection has two important advantages in projecting crystals:

(1) any circle drawn on a sphere will be projected also as a circle;

(2) the angle between two arcs of great circles on a sphere is equal to the angle between the same arcs in stereographic projection.

Let us take a circle K_1 on a sphere (Fig. 39, *a*). It is projected as a curve $K'_1P'_1P$. It must be proved that the curve is a circumference.

P_1P_2, and $P'_1P'_2$ will be the respective diameters. From an arbitrarily chosen point K'_1 of the curve $K'_1P'_1P$ we drop a perpendicular PI to the $P'_1P'_2$ diameter.

By proving that $(PI)^2=P'_1I \cdot P'_2I$ we shall prove that $K'_1P'_1P$ is the second circular section of the oblique round cone SP_1P_2,

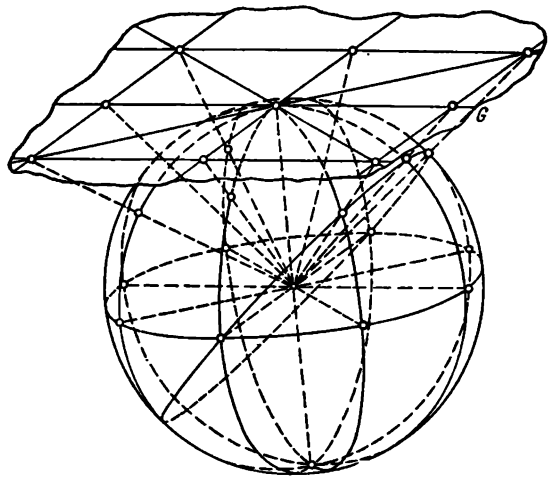


Fig. 37. Plotting a gnomonogram from a spherical projection

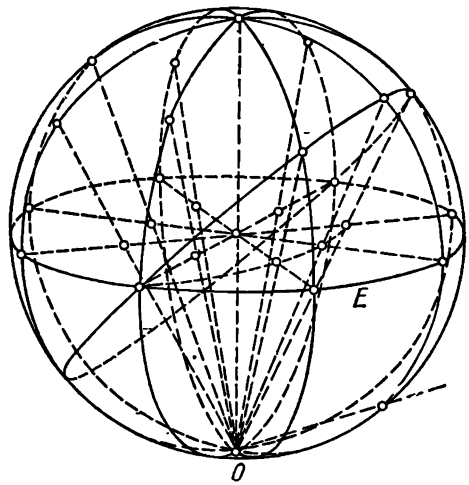


Fig. 38. Plotting a stereogram from a spherical projection

the first circular section of which is K_1. We draw a section Q_1Q_2 parallel to P_1P_2 through PI in the cone.

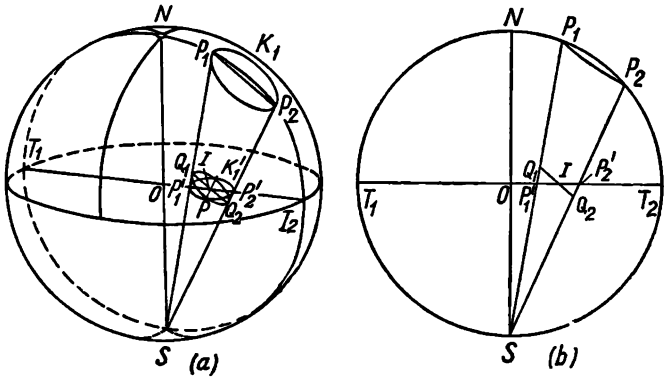


Fig. 39. Stereographic projection of a circle on a sphere

The triangles SP_1P_2 and $SP_1'P_2'$ (Fig. 39, *b*) are similar, since they have a common angle with the apex S, and the two other angles are equal to each other:

$$\angle SP_1'T_2 = \angle SP_2P_1 \text{ and } \angle T_1P_2'S = \angle SP_1P_2.$$

Triangles SP_1P_2 and SQ_1Q_2 are also similar. Therefore triangles $P_1'Q_1I$ and $P_2'Q_2I$ must also be similar.

Hence, we have:

$$\frac{P_1'I}{Q_1I} = \frac{Q_2I}{P_2'I},$$

or

$$P_1'I \cdot P_2'I = Q_1I \cdot Q_2I.$$

Since

$$Q_1I \cdot Q_2I = (PI)^2,$$

then

$$P_1'I \cdot P_2'I = (PI)^2,$$

which proves the case.

The second theorem is proved as follows. We are given two great circles K_1 and K_2 on a sphere (Fig. 40, *a*), their stereographic projections being $K_1'R_1$ and $K_2'R_2$. The point of intersection P of the circles K_1 and K_2 is projected at P_1. The angle between K_1' and K_2' must be proved to be equal to the corresponding angle between $K_1'R$ and $K_2'R$. Through the point of intersection P of the two circles let us draw a third great circle K_0 passing through the poles N and S of the sphere. On the plane Q which is tangent to the sphere at the point P we draw straight lines B_1P, B_0P, and B_2P which will be

tangent to the corresponding arcs, and the angle between K_1 and K_2 should be equal to the angle B_1PB_2. From the section of the sphere in the great circle K_0 (Fig. 40, *b*) we see that the triangle B_0PP_1 is isosceles; therefore by superposing the plane Q on the projection

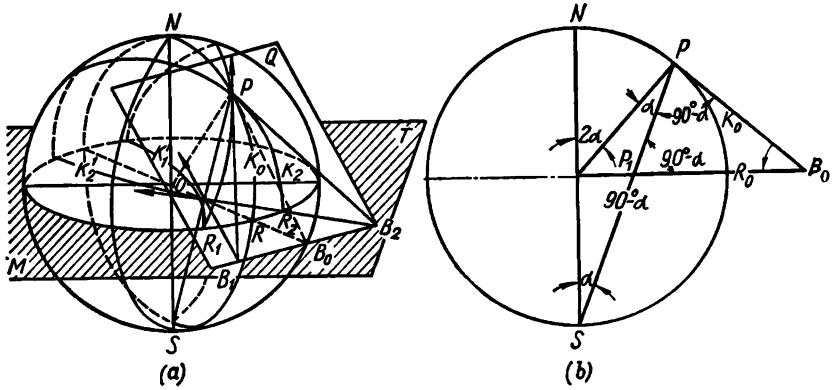


Fig. 40. A drawing to the theorem concerning the angle between arcs:
(*a*) construction in space; (*b*) cross-section on the plane of the circle NPR_0S

plane MT (Fig. 40, *a*) so that their line of intersection B_1B_2 remains in place, we shall superpose points P and P_1, while the tangential lines B_1P and B_2P will produce on the plane MT lines B_1P_1 and B_2P_2 which will be tangent to the projections $K_1'R_1$ and $K_2'R_2$ of the arcs K_1 and K_2. Because the angles between the tangents are equal, the angles between the arcs and their projections should also be equal.

Besides the described principal types of projections which accurately represent the angular relationship between crystal faces, there is a third type of projection—*axonometric*—which allows one to represent the external form of a crystal in a three-dimensional drawing with the point of vision at infinity. All the parallel edges of a crystal remain parallel on such a drawing. An axonometric projection can be drawn very accurately on the basis of a gnomonic or stereographic projection made earlier. The relative advantages and disadvantages of the projections described are as follows.

Both the stereographic and the gnomonic projections are very convenient for the treatment of the results of measurement of crystals, while the axonometric projection gives an accurate picture of crystal habit. The gnomonic projection gives central angles, the stereographic projection—inscribed angles (Fig. 41). If the two angles rest on the same arc (see Fig. 41), the inscribed angle will be half as large as the central angle. Therefore, if in the vicinity of the uppermost point of the pole of a sphere (N in Fig. 41), i.e., at the top of

a crystal, there is a large number of faces, the stereographic projection will give a less clear picture than that which the gnomonic projection can produce, since the latter moves the poles of these faces apart, as it were. On the other hand, faces with poles 90° distant from the point *N* will not get into the gnomonic projection, because the lines that connect them with the centre of the sphere will be parallel to the plane of projection. However, such faces do not create difficulties in projecting because the direction of their normals can be shown with arrows on the drawing (Fig. 42). It is much more difficult to work with faces whose polar distances are close to 90°, for instance, 80-85°. In such cases the normals to the faces intersect the plane of projection at a considerable distance from its centre, so that a very large drawing is required (Fig. 43).

In the USSR crystallographers mainly use the stereographic projection. The German crystallographer V. Goldschmidt and his followers prefer the gnomonic projection.

The treatment of the results of measurement of crystals, which was mentioned earlier, consists in determining the constants of crystals and the values of symbols characterizing the arrangement of their faces. These terms will be clear on studying Chapter VI of this book. Here we shall briefly describe the procedure used in finding them.

We can calculate the constants of a crystal and the symbols of its faces either trigonometrically or graphically from the values of angles obtained in measurement. Trigonometrical calculations give more accurate results but are much more labour-consuming. The second method gives less accurate results, but very often the accuracy obtained is quite sufficient. The procedure for graphical calculation has been developed by G. V. Wulff, who used a stereographic net of his own invention, which has since come into world-wide use. It makes graphical calculations very simple and easy. It seems appropriate to say here a few words about the advantages and disadvantages of nets designed by various authors.

What is a stereographic net? Imagine a sphere which, like a geographical globe, has meridians and parallels drawn across it. A stereographic projection of such a sphere can obviously be made in the same manner as a projection of a crystal.

If we take a point of vision in one of the poles, we shall have a net like the one in Fig. 44. This is a so-called polar net. If the point of vision is placed at the equator, an equatorial-type net will result (Fig. 45). The polar net allows easy plotting of angles from the centre and along concentric circumferences, but it does not allow the measurement of angles between arbitrary points within a circle. The equatorial net solves this problem, which is most essential for practical crystallography, and at the same time it is a good substitute for the polar net. Therefore at present all plotting is done

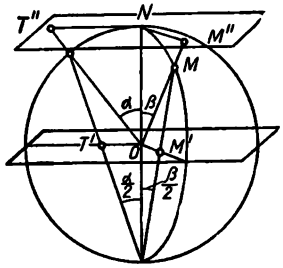


Fig. 41. Relationship between angles in stereographic and gnomonic projections

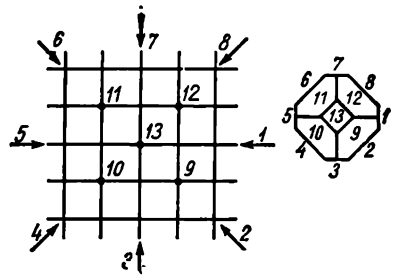


Fig. 42. Gnomonic projection of a viluite crystal

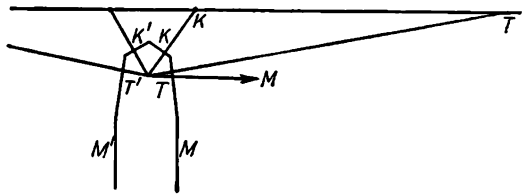


Fig. 43. Gnomonic projection of a face with a large polar distance ρ

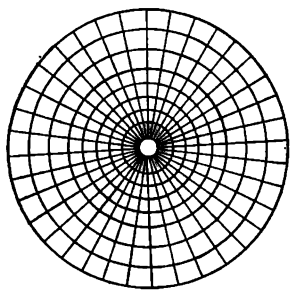


Fig. 44. A polar-type net

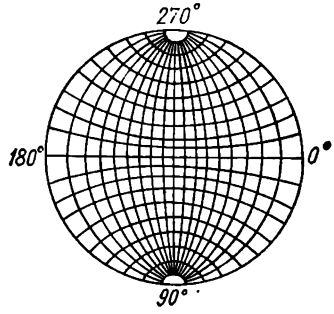


Fig. 45. An equatorial-type net

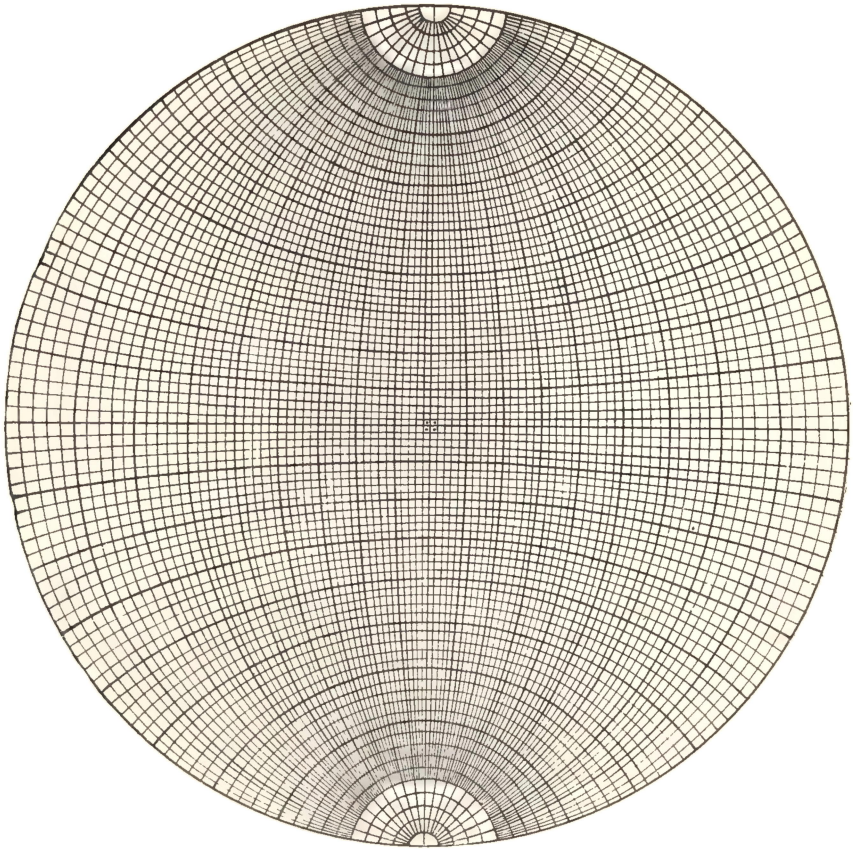


Fig. 46. Wulff net

on the equatorial net as suggested by G. V. Wulff. It is usually 20 cm in diameter, graduated in two-degree divisions, and for convenience in taking readings every tenth meridian and every tenth parallel are drawn in bold lines (Fig. 46).

This net is plotted in the following manner. A circle 20 cm in diameter is drawn. Its circumference is divided into four parts by two mutually perpendicular diameters AA_1 and BB_1 (Fig. 47). Each of these parts is divided into 9 parts (a convenient procedure is to divide each part into 3 parts and further subdivide these into 3 parts). Thus, the circumference will be divided into 36 equal arcs of 10 degrees each. When each arc is divided into 5 parts, the final (2°) divisions of the net are obtained. It has already been mentioned that the Wulff net is a stereographic projection of a sphere divided

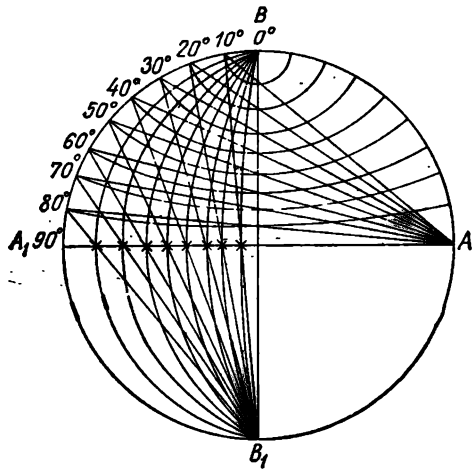


Fig. 47. Construction of the Wulff net

into degrees by meridians and parallels. Therefore, we must construct it in the same manner in which we projected the face poles of a crystal. With the point of vision at B_1 we shall find the projections of points 0°, 10°, 20°, etc., on the diameter AA_1. To avoid making too complicated a drawing, the division of the circumference in Fig. 47 has been shown in increments of 10°, and the meridians and parallels have been projected on only half of the circumference. The points of intersection of the lines of sight drawn from B_1 with the diameter AA_1 determine the points of the respective meridians on the projection. We have two points for each meridian at the poles B and B_1. Therefore, using the three points, we can project the meridians (great circles). Having moved the point of vision to A and made similar construction on the diameter BB_1, we shall have the projections of the parallels (small circles). Two points for each of them lie on the circumference of the primitive circle, and the third point is located at the intersection of the corresponding line of sight with the diameter BB_1.

Fedorov suggested the use of a net (Fig. 48) in which one polar net is combined with two equatorial nets turned by 90° with respect to each other. The arcs of great and small circles are drawn every five degrees. A projection is plotted on the net itself, as contrasted to the Wulff net, which is used in making a projection on tracing paper superimposed on the net. The Fedorov net is less convenient than the Wulff net, because the great number of lines and arcs on it creates confusion and wearies the eye. Moreover, the accuracy of readings

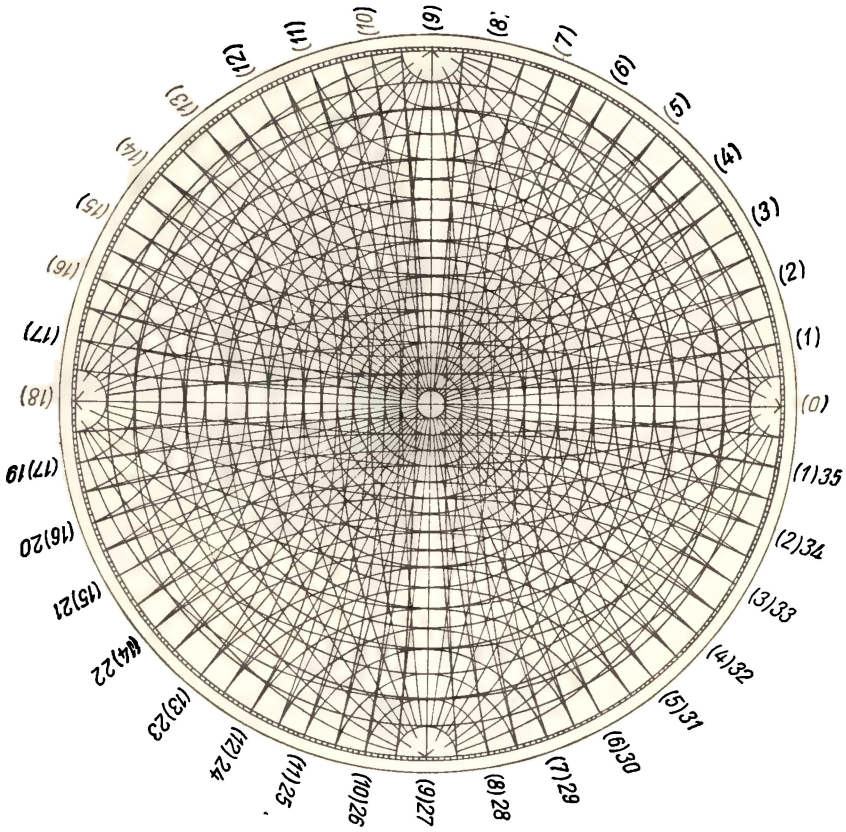


Fig. 48. Fedorov net

with the Fedorov net is not as high as with the Wulff net, since the distance between arcs is five degrees, and not two.

The Boldyrev net (Fig. 49) is a polar net with two-degree divisions. It is very convenient in plotting results of measurements obtained in the form of spherical coordinates ρ and φ.

The net designed by Flint (Fig. 50) is a combination of the Wulff and Boldyrev nets, each of which has been cut in two. The polar half with two-degree divisions is used for plotting the results of measurements. The projection is made on tracing paper which can be rotated about an axis perpendicular to the plane of the net; thus, half a net can be used as a complete one. The second part, which is a half of the Wulff net, can be used for solving on tracing paper of all problems occurring in graphical calculations of crystals.

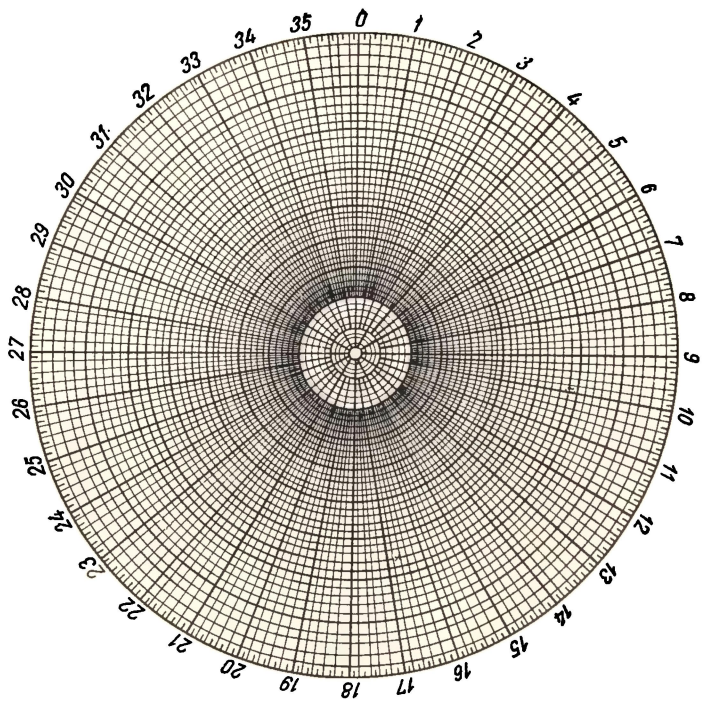


Fig. 49. Boldyrev net

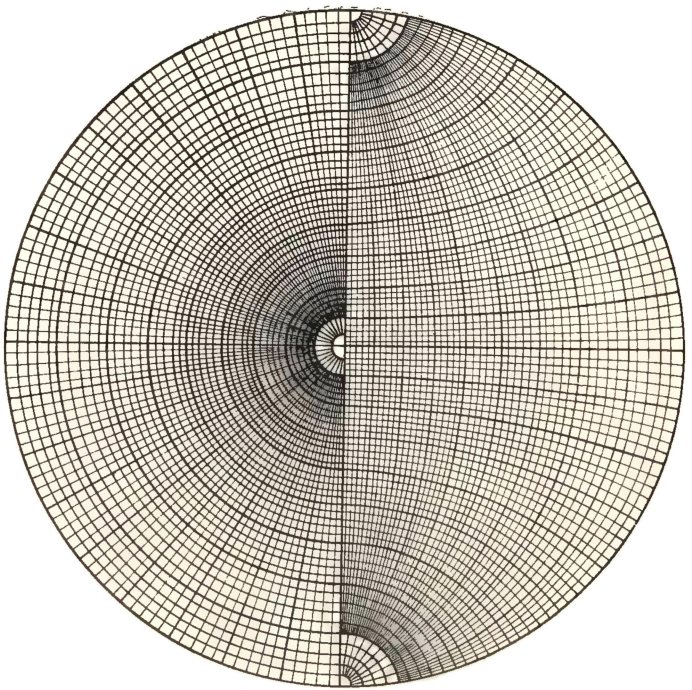


Fig. 50. Flint net

CHAPTER IV

The Concept of Symmetry of Crystals

Symmetry is a peculiar regularity observed in the arrangement of objects or parts thereof on a plane and in space. Nowhere else in nature is symmetry revealed in such richly varied forms as in crystals. It is their characteristic feature which serves as a basis for their classification.

Any geometrical body, as well as any plane figure, can be regarded as a combination (or a system) of points.

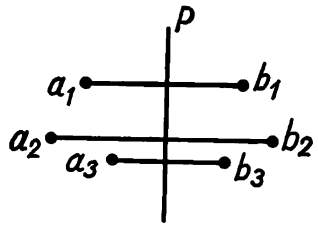


Fig. 51. Plane of symmetry

Any two figures are *mutually symmetrical* if they will coincide when matched. If a figure has two equal coincident parts, it is auto-symmetrical. Transformations or operations of matching two symmetrical figures or two parts of an auto-symmetrical figure are called *symmetry operations*. The geometrical expression of such a symmetry operation is called an *element of symmetry*.

There are several symmetry operations, some of which relate to finite figures, and others to infinite images. This chapter deals with the former, and Chapter XIII with the latter.

1. Reflection Through a Plane. If we take a system of points, say, a_1, a_2, a_3 (Fig. 51) and reflect them through a plane P as in a mirror, we shall have a new system of points: b_1, b_2, b_3, which will be symmetrical with the original group. The element of symmetry in this operation is a symmetry plane designated by the letter P or m.

The symmetry plane divides a figure into two equal parts which cannot always be matched by simple superposition. Therefore it is necessary to distinguish two types of coincidence: (a) *congruent equivalence*, when figures are matched by superposition or insertion, and (b) *mirror-equivalence*, when superposition is possible only upon reflection of one of the figures in a mirror. The right and the left hands are an example of the latter type of equivalence (Fig. 52). Two mirror-equivalent figures are *enantiomorphous.*

A figure can have one or more symmetry planes. In the latter case their number is indicated by a coefficient cipher before P.

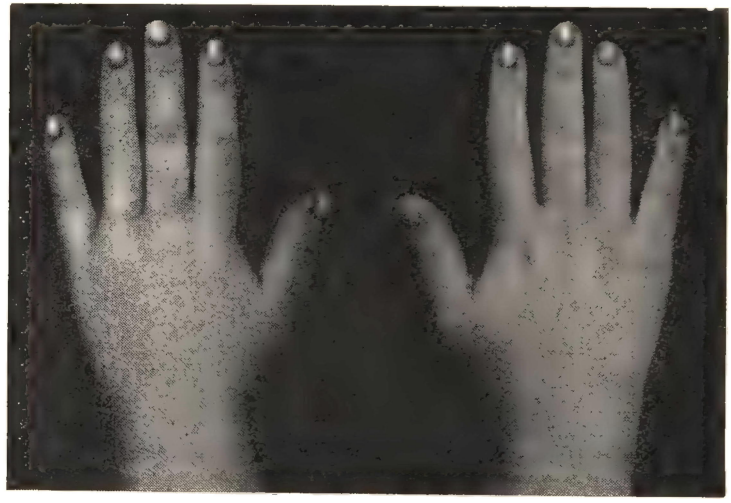


Fig. 52. An example of enantiomorphous figures

2. Rotation. By rotating a figure through a certain angle it can be turned into a congruent position. The axis of rotation is then called an *axis of symmetry* and is an element of symmetry in rotation. The angle of rotation should be an aliquot part of 2π or of 360°.

Repetition is sometimes obtained by rotating a figure through different angles. The least of the angles is called an *elementary angle of rotation.*

For instance, a regular hexagon can be turned into congruent positions by rotation about a perpendicular axis passing through the point of intersection of its diagonals, each of which is equal to $2R$. The hexagon will turn into a congruent position after rotation through 60°, 120°, 180°, and 360°. The angle of 60° is elementary for this axis of symmetry.

The denomination or the order of the n axis is related to the elementary angle α as follows:

$$n = \frac{360^\circ}{\alpha}.$$

The symmetry axis is designated by the letter L or g or simply by a cipher. The order number of the axis is placed above or below the letter, usually to the right of it. For instance, a symmetry axis with an elementary angle of 90° is denoted by L^4 or g^4 or simply by 4, and is called a fourfold symmetry axis.

Geometrical figures may have axes of any degree. Crystals, because of their reticular structure, can have the following axes: L^1, L^2, L^3, L^4 and L^6. On stereographic projections they are designated by the following symbols:

Degrees of symmetry—5 and those higher than 6, are not possible, as can be proved by the following.

Let us imagine an L^5 axis in a crystal (Fig. 53), and take the nearest lattice node, a_1. A plane net of the lattice containing node a_1 should be normal to the axis.

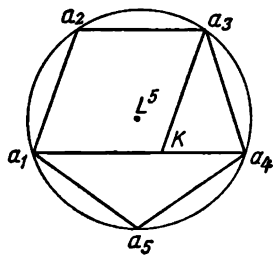


Fig. 53. A drawing to the theorem concerning the impossibility of a fivefold axis

Having performed the operation necessary for a fivefold symmetry axis, i.e., rotation through 72°, we find the consecutive points a_2, a_3, a_4 and a_5. By connecting points a_1 and a_4 we get a line parallel to the side a_2a_3 of a regular pentagon.

All parallel rows in a lattice have identical spacings between nodes. Therefore, if we plot on the line a_1a_4 a segment equal to a_2a_3, we shall have a node K inside the pentagon which will be closer to L^5 than any of the points a_1, a_2, a_3, etc. Thus, we arrive at a conclusion which defeats our postulate that a_1 must be the nearest point to L^5. Hence a fivefold axis in a crystal is impossible. Similarly, it can also be proved that degree of symmetry, n, cannot exceed 6.

There is another explanation why a fivefold axis is impossible.

A plane net should lie perpendicularly to the symmetry axis in a space lattice. The loops that are built up between the nodes of the net must have a symmetry corresponding to the degree of symmetry of the axis. For instance, the loops of a net perpendicular to a twofold axis should be polyhedra coming into a congruent posi-

tion on rotating through 180°. Therefore, the loops of a plane net perpendicular to a fivefold axis would have to be regular pentagons. A plane cannot be continuously filled, however, with regular pentagons, i.e., no number of pentagons can be fitted together so that their apexes would meet at a common point, because the angle of a regular pentagon is 108°, which is not a quotient of 360°. The same would be the case if the value of n were 7, 8, and so on.

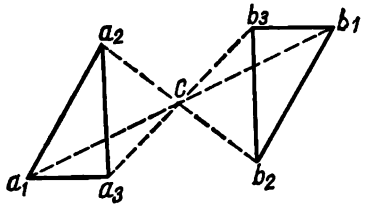


Fig. 54. Centre of inverse equality

3. Inversion. This is a symmetry operation similar to reflection, with the only difference that reflection occurs in the plane of the mirror, while inversion is equivalent to reflection through a point—the centre of symmetry, which is also the symmetry element in the operation of inversion.

Figure 54 shows the relevant construction. All the points of a triangle including its apexes a_1, a_2, a_3 produce by reflection through point C a new triangle $b_1b_2b_3$ which is symmetrical with the first one. Point b_1, for instance, is plotted from point a_1 in the following manner: a_1 is connected to C by a line which is then produced by a segment $Cb_1=a_1C$. The figure thus obtained is inverted.

In a crystal with a centre of symmetry each face has its counterpart—a parallel inverted face; therefore the centre of symmetry is also called the *centre of inverse equality*. The final figure can have only one centre of symmetry.

4. Rotoreflection. In this operation a congruent position is assumed by a figure through simultaneous rotation about a given axis L and reflection through a mirror plane M. The rotoreflection axis is a symmetry element. To enable one to understand the operation more clearly, let us perform rotation and reflection consecutively.

Figure 55 shows a sixfold rotoreflection axis L_6^3. A point a_1 is rotated through 60° about this axis and arrives at a point b_1. Next we reflect the point b_1 through a plane perpendicular to this axis: the point b_1 will occupy the position a_2. By repeating the operation we shall produce points a_2, a_3, a_4, etc. As a result of the last turn and reflection, the point b_6 will coincide with the initial point a_1.

It can be seen from Fig. 55 that in the operation with the sixfold rotoreflection axis the points a_1, a_3, a_5, i.e., those with odd numbers, are above, while a_2, a_4, a_6 are below.

Coincidence could be obtained without reflecting the figure through a plane, but then it would be necessary to rotate it through twice as large an angle (120°). It follows, therefore, that a *rotoreflection axis of an even number is at the same time a simple axis of symmetry*

of half the number. In stereographic projection the relevant designations are:

The same letter L is used, but with two ciphers: one below for rotoreflection, and one above for simple rotation (L_{2n}^{n}).

Figure 56 shows the result of the operation on the L_6^3 axis.

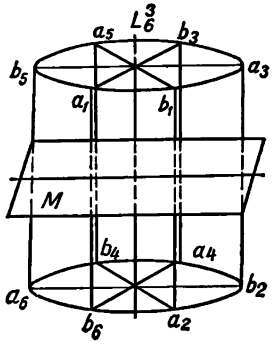


Fig. 55. Result of the action of a rotoreflection axis

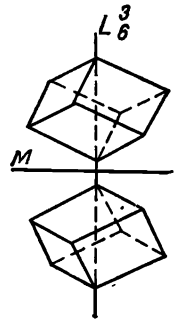


Fig. 56. Result of the action of the L_6^3 axis on a rhombohedron

Symmetry operations for images of infinite extension—translation, screw axis, and glide plane, will be discussed later.

5. Rotoinversion. This operation is analogous with the preceding one, the only difference being that after rotation about an axis, reflection is not through a plane, but through a point. A combination of rotation and inversion is thus obtained. The symmetry element in this operation is an *inversion axis* designated as L_i or G_i, the degree being shown either above, e.g., L_i^1 or below, G_{i4}. The following inversion axes can be met in crystals: L_i^1, L_i^2, L_i^3, L_i^4, L_i^6, where $L_i^1=C$, $L_i^2=P$, and L_i^3 corresponds to the combination of L^3 and C. Thus, only L_i^4 and L_i^6 have an importance of their own.

In the following discussion we shall make use of the rotoreflection axis.

COMBINATION OF SYMMETRY OPERATIONS

If a figure has several symmetry elements, they should be related to each other in a definite manner. Let us analyse a few simple cases.

Theorem 1. When a figure has two or more symmetry planes (P), the lines of their intersection are *symmetry axes* (L). The elementary angle of rotation of the respective axis is twice the angle at which the planes intersect.

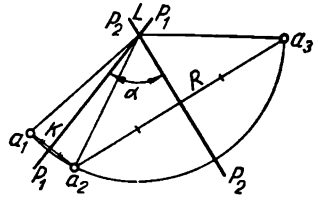


Fig. 57. A drawing to the Theorem 1

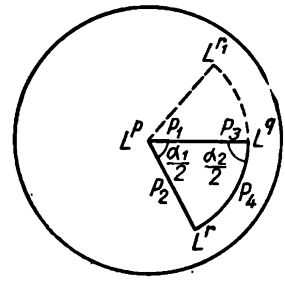


Fig. 58. A drawing to the Theorem 2

Figure 57 shows planes P_1 and P_2 perpendicular to the plane of the drawing. They intersect at an angle α. The line of their intersection, which is a symmetry axis with an elementary angle 2α, must pass through the point L. Let us take an arbitrary point a_1 on the plane and obtain two consecutive reflections of it, points a_2 and a_3, through the planes P_1 and P_2. The combined action of the two symmetry planes has caused point a_1 to move to a_3. Let us draw lines a_1a_2 and a_2a_3; they will cut the planes P_1 and P_2 at points K and R. By connecting the points a_1, a_2, a_3, K, and R with L we shall obtain four right triangles a_1LK, a_2LK, a_2LR, a_3LR with $a_1LK = a_2LK$, and $a_2LR = a_3LR$. From this we see that $a_1L = a_2L = a_3L$. Therefore, points a_1, a_2, a_3 all lie on the same circumference, and the point a_1 can be made to coincide with a_3 by rotating it through the angle a_1La_3 about the axis L. This angle is double the intersection angle of the planes P_1 and P_2, because $a_1LK = a_2LK$ and $a_2LR = a_3LR$, and $a_2LK + a_2LR = \alpha$.

The following conclusions can be drawn from the above proof:

(a) the action of a symmetry axis can be replaced by the combined action of two planes intersecting along it;

(b) when a figure has a symmetry plane P_1 with a symmetry axis L^n in it, this figure must also have a second plane P_2 intersecting P_1 along the axis L^n at an angle determined by the degree of the axis.

Theorem 2. When a figure has two axes of symmetry: L^p with an elementary angle α_1 and L^q with an elementary angle α_2, it must have a resultant axis L^r (Euler's theorem).

Let us take initial axes in stereographic projection (Fig. 58).

Only their degree and intersection angle are mandatory, while their arrangement in space is quite arbitrary. Let us then place the termination of axis L^p in the centre, and that of L^q at the right at a given angle. On the basis of the conclusion (a) of the Theorem 1 we can replace the L^p axis with two planes P_1 and P_2 intersecting at an angle $\frac{\alpha_1}{2}$. One of the planes (P_1) is made to pass through L^q. Thus, we have two symmetry planes P_1 and P_3.

Let us make a similar replacement for L^q obtaining symmetry planes P_3 and P_4, the former being drawn through L^p and the latter will be disposed at an angle of $\frac{\alpha_2}{2}$ to P_3. The combined action of planes P_1 and P_3 is equivalent to zero, since consecutive reflection in two coincident mirror planes returns the point to its initial position. The remaining planes are P_2 and P_4. The line of their intersection should be an axis of symmetry L^r, the resultant of L^p and L^q.

Without changing the degrees of the axes or the angle between them we could plot angles $\frac{\alpha_1}{2}$ and $\frac{\alpha_2}{2}$ in the reverse direction (broken lines in Fig. 58) and obtain a second resultant symmetry axis L^{r_1}. Thus, the initial axes of L^p and L^q have, strictly speaking, two symmetrically arranged resultant axes.

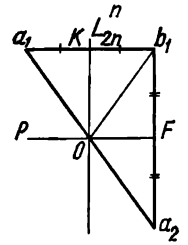


Fig. 59. A drawing to the Theorems 3 and 4

Theorem 3. The point, at which a symmetry axis of an even degree cuts a plane that is perpendicular to it, is a centre of symmetry.

Let us take L^n_{2n} (Fig. 59) as an axis of an even degree with plane P perpendicular to it. An arbitrary point a_1 will occupy the position b_1 after rotation through 180°. With n an even number such a rotation is always possible, since the number of elements into which n can be factorized always includes 2, for which the angle of rotation is 180°. On reflection through a plane, b_1 becomes a_2.

Having connected points a_1, b_1 and a_2 with the point of intersection of the axis and the plane (O) we obtain two pairs of equal right triangles, i.e., $a_1KO=b_1KO$, $b_1FO=a_2FO$. It can be seen that $a_1O=b_1O=a_2O$. The sum total of angles at the point O is 180°; therefore, a_1Oa_2 is a straight line, and $a_1O=a_2O$, i.e., the point O is the centre of inverse equality.

Theorem 4. A centre of symmetry is equivalent to an infinite number of twofold rotoreflection axes, i.e., $C=\infty L^1_2$. Rotation through 180° followed by reflection through a plane will transfer point a_1 to a_2 (Fig. 59).

It has been proved above (Theorem 3) that O is a centre of sym-

metry. The initial position in space of the L_2^1 axis with a plane perpendicular to it can be chosen arbitrarily. Therefore, the number of axes passing through the point O is infinite.

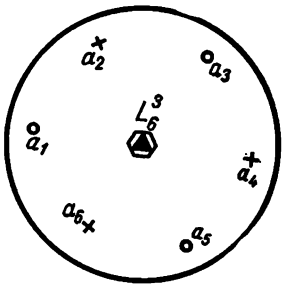


Fig. 60. A drawing to the Theorem 5

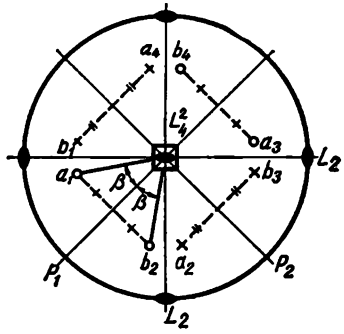


Fig. 61. A drawing to the Theorem 6

Theorem 5. The presence of a rotoreflection axis L_{2n}^n, where n is an odd number, always involves the presence of a centre of symmetry.

This rule is obvious from the diagram in Fig. 60 and from the Theorems 3 and 4 above. Let the termination of the L_6^3 axis be at the centre of projection. Then the point a_1, on rotation through 60° and reflection through a plane, will occupy positions a_2, a_3, a_4, a_5 and a_6. For each point in the upper hemisphere there is a diametrically opposite point in the lower one (crosses in Fig. 60). Therefore, there is a centre of inverse equality at the point of intersection of L_6^3 and the plane of projection.

This construction is true for any L_{2n}^n axis with an odd n.

Theorem 6. When a rotoreflection axis L_{2n}^n, where n is an even number, is combined with a twofold symmetry axis which is perpendicular to it, we obtain n symmetry planes passing through L_{2n}^n.

Let us take an L_4^2 axis in the centre of a projection and an L^2 axis normal to it (Fig. 61). On rotation through 90° we shall obtain another twofold axis, i.e., a total of two twofold axes—$2L^2$.

An arbitrary point a_1 will occupy, due to the action of the L_4^2 axis, positions a_1, a_3 in the upper hemisphere, and a_2, a_4 in the lower one. The twofold axes ($2L^2$) will transfer these points into positions b_1 to b_4.

It can easily be proved that the points a and b are symmetrical reflections with respect to the two planes P_1 and P_2 which intersect along the L_4^2 axis and bisect the angles between the L^2 axes.

The theorems discussed are necessary for the derivation of all the possible combinations of symmetry elements in a crystal.

CHAPTER V

Derivation of All Possible Crystal Classes

A crystal class is a combination of symmetry operations in which all the resultant elements of symmetry have been derived. For instance, $2P$ is not a crystal class, since a symmetry axis L^2 should appear as a result of a combination of two symmetry planes if they intersect at right angles. The crystal class in this case will be $L^2 2P$.

All crystals with an external form of the same symmetry constitute a *class.*

Symmetries and accordingly crystal classes have definite denominations and symbols which differ widely with different authors. We shall use the simplest and the most easily remembered ones.

The derivation of all possible crystal classes was first made by Hessel in 1830. Later many authors (Fedorov, Bravais, Curie, Wulff) arrived at the same results in different ways. We shall cite the derivation made by the Russian scientist A. V. Gadolin (1867) somewhat adjusted for the sake of simplicity.

Basically, we have the following elements of symmetry possible in finite figures:

(1) plane of symmetry P;
(2) axes of symmetry L^1, L^2, L^3, L^4 and L^6;
(3) rotoreflection axes $L_2^1=C$, L_4^2, and L_6^3;
(4) centre of symmetry C.

In investigating all the possible combinations of these elements we shall divide them into two groups, A and B. Group A will include the crystal classes in which after the addition of symmetry elements there will be *only one symmetry axis of the higher degree,* and group B will include those with *several* L^n *axes* with n greater than 2.

The derivations for each group are of a specific nature, and it is therefore best to give them separately. We shall begin with group A, remembering above all that no symmetry in its class can have more than one symmetry axis of the higher degree.

1. Let us assume that the entire symmetry of a figure consists of only one symmetry axis of any denomination, L^n.

The following symmetries are then possible in crystals:

$$L^1,\ L^2,\ L^3,\ L^4,\ L^6.$$

In the general form we have L^n, where n can have values possible in bodies with a reticular structure. For geometrical figures n can be any whole number.

2. To avoid the appearance of a new axis of the higher degree, only an L^2 axis can be added to L^n. The former can only be in a position perpendicular to L^n (Fig. 62).

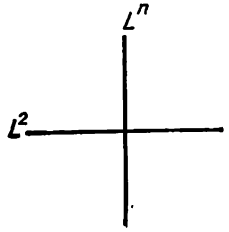


Fig. 62. Addition of an L^2 symmetry axis perpendicularly to an L^n axis

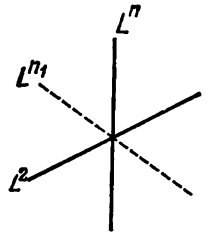


Fig. 63. Addition of an L^2 symmetry axis to an L^n axis at an oblique angle

In crossing L^n at an oblique angle a twofold axis will move L^n into a new position: L^{n_1} (Fig. 63). We shall have $2L^n$, which is impossible according to our condition. The L^2 axis added to L^n will not remain alone. On the basis of Euler's theorem of the addition of two rotation axes there must appear other L^2 axes as resultants. Their number depends on the value of the elementary angle of rotation of the main axis. If we have the main axis of the degree n, the number of L^2 axes will be n. Thus, the addition of L^n and a twofold axis normal to it results in symmetries L^nnL^2. We shall then have the following symmetries:

$$L^1L^2 = L^2;\ L^22L^2 = 3L^2;\ L^33L^2;\ L^44L^2;\ L^66L^2.$$

3. For group A symmetries a symmetry plane can be added to L^n either perpendicularly (Fig. 64) or parallel to the symmetry axis (Fig. 65).

In the first case we obtain the L^nP series. According to the Theorem 3 (Ch. IV) the point of intersection of an even-degree axis with a symmetry plane normal to it is a centre of symmetry.

We thus obtain the third series of symmetries:

$$L^1P = P;\ L^2PC;\ L^3P;\ L^4PC;\ L^6PC.$$

4. Adding a parallel symmetry plane to L^n, i.e., placing the axis in the plane, we should, according to the theorem of addition of planes, obtain another plane at an angle $\frac{\alpha}{2}$ to the first one. In accordance with the degree of the L^n axis there must appear $n-1$ more planes intersecting along this axis.

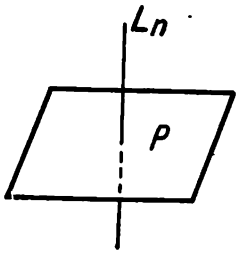


Fig. 64. Addition of a plane perpendicularly to an L^n axis

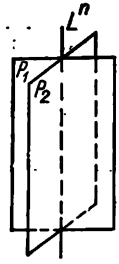


Fig. 65. Addition of a plane parallel to an L^n axis

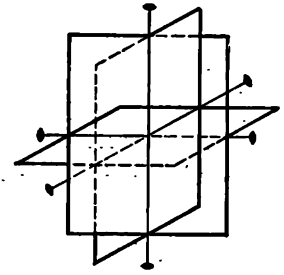


Fig. 66. Addition of a plane perpendicularly and parallel to an L^n axis

Therefore, the fourth series will contain the symmetries:

$$L^1P=P;\ L^22P;\ L^33P;\ L^44P;\ L^66P.$$

5. It has been said that symmetry planes can be added for the first group of symmetries only in directions parallel or perpendicular to the axis. But they can also be added in both ways simultaneously (Fig. 66). In this case we shall obtain the total of symmetry elements by summing the third and the fourth rows in each column of Table 1. Moreover, by adding to the L^n axis two symmetry planes

Table 1

Symmetries of group A

No.	General formula	Symmetries				
		$n=1$	$n=2$	$n=3$	$n=4$	$n=6$
1	L^n	L^1	L^2	L^3	L^4	L^6
2	L^nnL^2	$*L^1L^2=L^2$	$L^22L^2=3L^2$	L^33L^2	L^44L^2	L^66L^2
3	$L^nP_{\perp}\ (C)$	$L^1P=P$	L^2PC	L^3P	L^4PC	L^6PC
4	$L^nP_{\parallel}$	$*L^1P=P$	L^22P	L^33P	L^44P	L^66P
5	$L^nnL^2\ (n+1)\ P\ (C)$	$*L^1L^22P=L^22P$	$L^22L^23PC=3L^23PC$	L^33L^24P	L^44L^25PC	L^66L^27PC
6	$L^n_{2n}\ (C)$	$L^1_2=C$	L^2_4	L^3_6C	—	—
7	$L^n_{2n}nL^2nP(C)$	$*L^2PC$	$L^2_42L^22P$	$L^3_62L^23PC$	—	—

at an angle of 90°, we cause to appear new axes of the second degree ($\alpha=180°$).

How many axes of this degree will there be? There will be as many as there are vertical planes, that is n.

We derive the fifth series of symmetries:

$$L^1L^22P;\ 3L^23PC;\ L^33L^24P;\ L^44L^25PC;\ L^66L^27PC.$$

All the combinations of rotation axes and symmetry planes for the group A have been exhausted. We shall now have to deal with rotoreflection axes.

6. The sixth series consists of symmetries that have only one rotoreflection axis L^n_{2n}. C appears when n is odd. Therefore, we shall have the following series of symmetries:

$$L^1_2=C;\ L^2_4;\ L^3_6C.$$

Axes of higher degree are impossible in crystals.

7. Combining rotoreflection axes with an L^2 axis normal to them (Fig. 67), we obtain in accordance with Theorem 6 of Chapter IV (see page 61) n vertical planes: $L^n_{2n}nL^2nP(C)$.

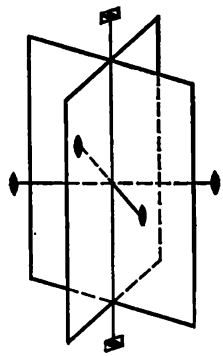


Fig. 67. Addition of a twofold axis to a rotoreflection axis

The seventh series of symmetries will appear as follows:

$$L^1_2L^2P=L^2PC;\ L^2_42L^22P;\ L^3_63L^23PC.$$

We have obtained altogether 31 symmetries, but some of them appear twice (in Table 1 they are marked with an asterisk). There are four such symmetries, hence group A contains 27 different crystal classes.

Before dealing with the second group (B) we should first answer the question: is the combination of a finite number of axes of the higher degree possible? By way of explanation let us analyse a simple case: L^3 and L^4 intersect at an arbitrary angle.

L^3 and L^4 are symmetry axes independent of the appearance of the resultant rotation axes (in accordance with Euler's theorem). Therefore, around L^3 there must be two more L^4 axes, besides the given L^4, which coincide on rotating through 120°. The same applies to an initial L^4 axis, i.e., besides the given L^3 it must have three more axes of the third degree so that the whole system will assume a congruent position at each 90° turn. Thus, from two symmetry axes intersecting at an arbitrary angle we obtain $3L^4$ and $4L^3$, i.e., seven axes. But the considerations just mentioned are true with respect to each of the new axes, so that the number of axes will not be seven, but much greater.

The appearance of each of the new axes is followed by an endless number of new axes. Can this development of new axes stop? If so, how? We may answer that *either the number of axes will grow infinitely and we shall arrive at the symmetry of a sphere having* $\infty L^{\infty} \infty PC$, *or the new and resultant axes will coincide with the earlier ones and thus will be finite in number.*

To answer this question more decisively, we shall assume that the problem has already been solved, and that on the basis of two axes of a degree higher than 2 we have obtained a finite number of symmetry axes intersecting at a certain point. How are we to determine their number, degree, and possible arrangement in space?

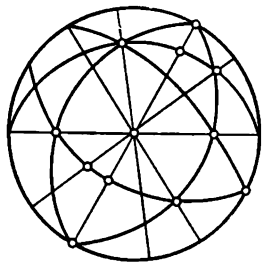


Fig. 68. Arbitrary arrangement of axes on a sphere

Let us describe a sphere around the point of intersection. On crossing the surface of the sphere, the axes will produce a spherical projection. Let us now draw a diametrical plane through each pair of points (Fig. 68). Each axis can be regarded as the line of intersection of two symmetry planes. The angle between the planes will be half the elementary angle of the rotation of the axis. The whole sphere will be divided into spherical triangles. We can determine the possible angles of these triangles: at the points of termination of the axes two adjoining symmetry planes should intersect at an angle of $\frac{\alpha}{2}$.

Insofar as we are discussing combinations of the elements of symmetry possible only for crystals, the axes can be sixfold, fourfold, threefold, and even twofold. In halving the elementary rotation angles for these axes we obtain 30°, 45°, 60° and 90°, respectively.

From spherical trigonometry we know that the sum of the angles (S) of a spherical triangle must be within $180° < S < 180° \times 3$. Hence it can easily be seen what spherical triangles are possible in our case. As our examination concerns classes with several symmetry axes of a higher degree, a triangle must, therefore, have at least two apexes through which these axes pass, and only one apex can be considered to be outlet of a twofold axis as a possible resultant axis. Below are given the combinations of angles of a spherical triangle through two apexes of which axes of the higher degree must pass:

$$L^6 + L^6 + L^2$$
$$30° + 30° + 90° = 150°$$
$$L^4 + L^4 + L^2$$
$$45° + 45° + 90° = 180°$$

$$L^6 + L^4 + L^2$$
$$30° + 45° + 90° = 165°$$
$$L^4 + L^3 + L^2$$
$$45° + 60° + 90° = 195°$$
$$L^6 + L^3 + L^2$$
$$30° + 60° + 90° = 180°$$
$$L^3 + L^3 + L^2$$
$$60° + 60° + 90° = 210°$$

It can be seen from these combinations that (1) a sixfold symmetry axis can never pass through any angle of a spherical triangle, i.e., it can never be present in symmetries of group B; (2) possible spherical angles are those where $S=195°$ and $210°$, and consequently, axes L^4, L^3 and L^2, or L^3, L^3 and L^2 can pass through their apexes.

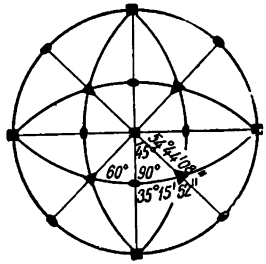


Fig. 69. Projection of symmetry elements of two classes with fourfold axes

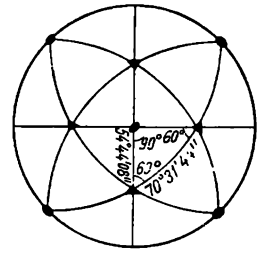


Fig. 70. Projection of symmetry elements for the class $3L_4^2\ 4L^3 6P$

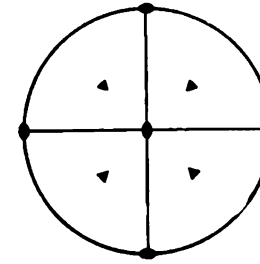


Fig. 71. Projection of symmetry elements for the class $3L^2 4L_6^3 3PC$

Knowing the angles, we can calculate the sides and construct the spherical triangles themselves. For the first triangle we obtain: side L^4—L^3=54°44′8″; side L^4—L^2=45°; and L^3—L^2=35°15′52″; for the second triangle, side L^3—L^3=70°31′44″, and side L^3—L^2= =54°44′8″.

If the surface of a sphere can be covered continuously with such triangles, their number and mutual arrangement will enable us to derive possible combinations of several axes of a higher degree. Having made the requisite markings, we see that in both cases the triangles fit the surface of the sphere continuously. In the first case we obtain the symmetry $3L^4 4L^3 6L^2$ (Fig. 69), and in the second $3L^2 4L^3$ (Figs. 70 and 71).

To the combination of axes $3L^4 4L^3 6L^2$ we add a symmetry plane in a manner which would not cause the appearance of new axes. Eight more planes appear. A $3L^4 4L^3 6L^2 9PC$ symmetry results.

For the second combination ($3L^24L^3$) the symmetry plane can be added in two ways: (1) so that it would pass through L^3 and L^2; thus, we obtain $3L^24L^36P$ (see Fig. 70); (2) so that it would pass only through the L^2 axes, bypassing the L^3 axes; thus, we obtain the last symmetry $3L^24L^33PC$ (see Fig. 71).

Hence, we have derived only five crystal classes for group B:

$$3L^44L^36L^2;\ 3L^44L^36L^29PC;\ 3L^24L^3;$$
$$3L^24L^36P;\ 3L^24L^33PC.$$

Thus, groups A and B contain a total of 32 possible crystal classes for the external form of crystals. In the second and fifth classes the threefold symmetry axes are rotoreflection axes of the sixth degree, and in the fourth class the L^2 axis becomes an L_4^2 axis.

CHAPTER VI

The Law of Rational Indices. Grouping of Crystal Classes into Systems. Orientation of Crystals

It was mentioned in Chapter I that the ability of a crystal to be covered with plane faces is the result of its reticular structure. The arrangement of faces depends on the direction of the rows in the crystal lattice and is governed by a very important law—the law of whole numbers, which is best known by the name of the law of rational indices.

The position of any crystal face in space can be designated by three whole numbers, if three crystal edges are used as coordinate axes and if the intercepts produced on these axes by the unit face are used as units of measurement.

If the directions of three rows of a lattice intersecting at one point are used as coordinate (reference) axes *I*, *II*, *III* (or *X*, *Y*, *Z*), any crystal face will cut one, two or all the three axes.

The following arrangement of reference axes in space is adopted in crystallography: axis *I*, or *X*, is directed towards the observer, axis *II*, or *Y*, extends from rignt to left, and axis *III*, or *Z*, is a vertical one.

The direction of each axis can be either positive or negative. Positive directions (from the origin) are as follows: for axis *I*(*X*)—towards the observer, for axis *II*(*Y*)—to the right, for axis *III*(*Z*)—upwards. The opposite directions are negative (see Fig. 72).

Insofar as each face must pass through the lattice nodes, it will intercept a certain whole number of row spacings on each axis. How is the size of these spacings to be determined?

X-ray examination of crystal structure (see Ch. XIII) will help us to find interatomic spacing in the three rows representing reference axes. If we do not use the X-ray method, we can take any face which cuts the three reference axes and measure or calculate the intercepts made by the face on the axes. The values obtained will always be proportional to the spacings to be determined. Consequently, we can establish their ratios, although the actual value of each will remain unknown.

Let us take the following example. Three lattice rows OX, OY, and OZ will serve as reference axes (Fig. 72). The faces $a_1b_1c_1$ and $a_2b_3c_6$ intercept certain segments on the axes: the first face intercepts segments Oa_1, Ob_1, Oc_1, and the second—Oa_2, Ob_3, Oc_6. We shall call these segments the *linear parameters of a face.*

If we assume that the first face intercepts one spacing in each row, then the second face will intercept two, three, and six spacings along the respective axes. We shall call the first face a *unit* face, as it makes one intercept on each axis, i..e., produces three values

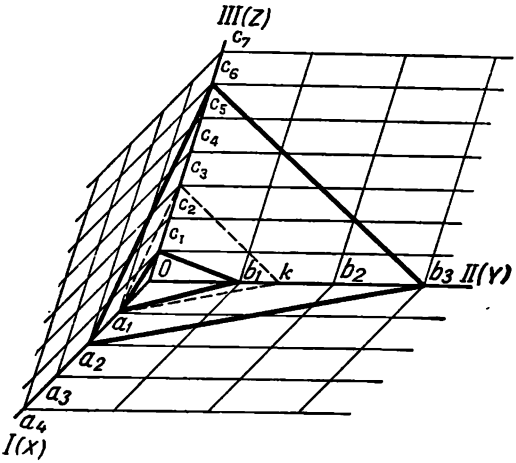


Fig. 72. Derivation of the law of rational indices

related to each other as 1 : 1 : 1. The second face produces $2a$: $3b$: $6c$=2 : 3 : 6. The figures 1, 2, 3, 6 are *numerical parameters of faces* and must always be whole numbers. It can be imagined that some face having passed through nodes on two axes will intersect the third axis between nodes and will not produce a whole number of spacings in the third row. The difficulty can be obviated by translating the face parallel to itself and finding such a position for it where it will pass through nodes on all three axes.

Face a_1kc_3 (see Fig. 72) illustrates the case. It passes through the nodes a_1 and c_3 on the axes I and III and intersects the axis II between the nodes b_1 and b_2. Having translated the face parallel to itself we find the position $a_2b_3c_6$ in which the face passes through the nodes on all the three reference axes.

Linear parameters intercepted by the unit face are called axial units and have permanent symbols: a on the axis I, b on the axis II, and c on the axis III. In the same way the angles between rows used

as reference axes are called *interaxial angles* and are designated by Greek letters: α is the angle between the axes *II* and *III*, β is the angle between the axes *I* and *III*, and γ is the angle between the axes *I* and *II*. These six values determine the shape of the lattice parallelepiped. The unit face is the solid diagonal of this parallelepiped (Fig. 73).

If we know the linear dimensions a, b, and c, and also the angles α, β, and γ, we know the form and the actual size of the parallelepiped. If we have no dimensions of the axial units, but only their ratio $a : b : c$ and the values of interaxial angles, we can determine only the form of the parallelepiped. Five values will suffice for this purpose, i.e., the interaxial angles α, β, γ and two values from the ratio $a : b : c$, since one of the values in this ratio can always be taken as unity. The ratio $a : b : c$ and the interaxial angles α, β, γ are called *geometrical constants of a given crystal substance.*

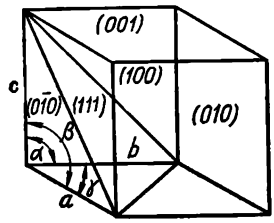


Fig. 73. An elementary parallelepiped and a unit face

Crystals are divided into systems according to the form of the parallelepiped. A system is a group of crystal classes which includes crystals with similar constants of the lattice parallelepiped. There are seven systems characterized by the following constants:

1. Cubic	$a=b=c;$	$\alpha=\beta=\gamma=90°$
2. Tetragonal	$a=b\neq c;$	$\alpha=\beta=\gamma=90°$
3. Orthorhombic	$a\neq b\neq c;$	$\alpha=\beta=\gamma=90°$
4. Monoclinic	$a\neq b\neq c;$	$\alpha=\gamma=90°;\ \beta\neq 90°$
5. Triclinic	$a\neq b\neq c;$	$\alpha\neq\beta\neq\gamma\neq 90°$
6. Trigonal	$a=b=c;$	$\alpha=\beta=\gamma\neq 90°$
(rhombohedral)	$(a=b\neq c;$	$\alpha=\beta=90°;\ \gamma=120°)$
7. Hexagonal	$a=b\neq c;$	$\alpha=\beta=90°;\ \gamma=120°.$

The angles are those between the terminations of the axes of the same sign.

The systems are often divided into three categories: (1) lower, which includes the triclinic, monoclinic, and orthorhombic systems; (2) intermediate, which includes the trigonal, tetragonal and hexagonal systems; and (3) higher, which consists only of the cubic system.

The 32 crystal classes derived above are grouped into systems, as shown in Table 2.

Several methods have been suggested for designating the crystal classes. These methods can be divided into two groups. The first group includes the symbols indicating all the symmetry elements in the class. In this case designations are very bulky and hard to pronounce, especially when the class contains a large number of symmetry elements. Moreover, they still fail to reflect the full complement of the symmetry elements of a crystal class. For instance, the sixfold symmetry axis L^6 is at the same time a threefold and a twofold axis, but the formula does not show it. The advantage of this method of designation is that the formulas contain all the principal symmetry elements of a class and are convenient at the early stages of studying symmetry. Therefore, they have been adopted as the principal symbols in this textbook.

The second group includes the methods of designation with symbols only for the basic elements of symmetry, i.e., those from which all the others can be derived. This method is suitable for persons who are sufficiently familiar with symmetry, and who can mentally make off hand all the additions and derive the resultant elements. Notations of this kind have been suggested by a number of authors. Those that are logically best founded are given in Table 2. They are often found in works on structural crystallography.

To understand the symbols better and to be able to memorise them more easily it is necessary to know the principle on which they are based. A few brief explanations are given below.

SCHOENFLIES NOTATION

Schoenflies denotes classes with one symmetry axis (L^2, L^3, etc.) by the letter C together with an appropriate numerical subscript, e.g., $C_2=L^2$, $C_3=L^3$, and so on. The letter C is the initial letter of the word *cyklisch*—circular, referring to the axis of rotation. The addition of a symmetry plane is denoted by a letter subscript next to the figure: if the plane is added normal to the axis, the letter h is used (*horizontal*), e.g., $C_{3h}=L^3P$; if the plane is parallel to the axis, the letter v (*vertikal*) is used, e.g., $C_{3v}=L^33P$. The letter D denotes classes with symmetry axes only (from the word *Diëder* whose meaning in geometry is different from that in crystallography). Thus, D_2 means $L^22L^2=3L^2$; $D_3=L^33L^2$.

Classes of the type L^44L^25PC are derived by Schoenflies from sphenoidal groups by the addition of a horizontal symmetry plane. Thus, $D_{4h}=L^44L^25PC$.

Classes with rotoreflection axes are denoted by the letter S (*Spiegelaxe*), i.e., a mirror axis, e.g., $S_4=L_4^2$.

And finally, classes with rotoreflection axes and twofold axes normal to them are denoted by D_{nd}, e.g., $D_{2d}=L_4^22L^22P$; $D_{3d}=L_6^33L^23PC$. A subscript i denotes inversion.

Table 2

Nomenclature and notation of the 32 symmetry classes

System and constants of its elementary parallelepiped	Description of class in the nomenclature of the Fedorov institute		Symmetry formula	Notation		
	as established in 1924	as established in 1935		Schoenflies	Hermann-Mauguin	Shubnikov
Triclinic $a \neq b \neq c$; $\alpha \neq \beta \neq \gamma \neq 90°$	1. Pedial 2. Pinacoidal	1. Primitive 2. Central	L^1 C	C_1 $C_i = S_2$	1 $\bar{1}$	1 $\bar{2}$
Monoclinic $a \neq b \neq c$; $\alpha = \gamma = 90°$; $\beta \neq 90°$	3. Sphenoidal 4. Domatic 5. Prismatic	3. Axial 4. Planal 5. Planaxial	L^2 P L^2PC	C_2 $C_{1h} = C_3$ C_{2h}	2 m 2/m	2 m 2:m
Orthorhombic $a \neq b \neq c$; $\alpha = \beta = \gamma = 90°$	6. Rhombic tetrahedral 7. Rhombic pyramidal 8. Rhombic bipyramidal	6. Axial 7. Planal 8. Planaxial	$3L^2$ L^22P $3L^23PC$	$D_2 = V$ C_{2v} $D_{2h} = V_h$	222 mm mmm	2:2 2·m m·2:m
Tetragonal $a = b \neq c$; $\alpha = \beta = \gamma = 90°$	9. Tetragonal pyramidal 10. Tetragonal trapezohedral 11. Tetragonal bipyramidal 12. Ditetragonal pyramidal 13. Ditetragonal bipyramidal 14. Tetragonal tetrahedral 15. Tetragonal scalenohedral	9. Primitive 10. Axial 11. Central 12. Planal 13. Planaxial 14. Gyroido-primitive 15. Gyroido-planal	L^4 L^44L^2 L^4PC L^44P L^44L^25PC L_4^2 $L_4^22L^22P$	C_4 D_4 C_{4h} C_{4v} D_{4h} S_4 $D_{2d} = V_d$	4 422 4/m 4mm 4/mmm $\bar{4}$ $\bar{4}2m$	4 4:2 4:m 4·m m·4:m $\bar{4}$ $\bar{4}$·m

Trigonal $a=b\neq c$; $\alpha=\beta=90°$; $\gamma=120°$ when set for 3 axes $a=b=c$; $\alpha=\beta=\gamma\neq 90°$	16. Trigonal pyramidal	16. Primitive	L^3	C_3	3	3
	17. Trigonal trapezohedral	17. Axial	L^33L^2	D_3	32	3:2
	18. Ditrigonal pyramidal	18. Planal	L^33P	C_{3v}	3m	3·m
	19. Rhombohedral	19. Central	L_6^3C	$C_{3i}=S_6$	$\bar{3}$	$\bar{6}$
	20. Ditrigonal scalenohedral	20. Planaxial	$L_6^33L^23PC$	D_{3d}	$\bar{3}$m	$\bar{6}$·m
Hexagonal $a=b\neq c$; $\alpha=\beta=90°$; $\gamma=120°$	21. Trigonal bipyramidal	21. Gyroido-primitive	L^3P	C_{3h}	$\bar{6}$	3:m
	22. Ditrigonal bipyramidal	22. Gyroido-planal	L^33L^24P	D_{3h}	$\bar{6}$2m	m·3:m
	23. Hexagonal pyramidal	23. Primitive	L^6	C_6	6	6
	24. Hexagonal trapezohedral	24. Axial	L^66L^2	D_6	62	6:2
	25. Hexagonal bipyramidal	25. Central	L^6PC	C_{6h}	6/m	6:m
	26. Dihexagonal pyramidal	26. Planal	L^66P	C_{6v}	6mm	6·m
	27. Dihexagonal bipyramidal	27. Planaxial	L^66L^27PC	D_{6h}	6mmm	m·6:m
Cubic $a=b=c$; $\alpha=\beta=\gamma=90°$	28. Tritetrahedral	28. Primitive	$3L^24L^3$	T	23	3/2
	29. Didodecahedral	29. Central	$3L^24L_6^33PC$	T_h	m3	$\bar{6}$/2
	30. Hexatetrahedral	30. Planal	$3L_4^24L^36P$	T_d	$\bar{4}$3m	3/$\bar{4}$
	31. Trioctahedral	31. Axial	$3L^44L^36L^2$	O	43	3/4
	32. Hexoctahedral	32. Planaxial	$3L^44L_6^36L^29PC$	O_h	m3m	$\bar{6}$/4

For the cubic system classes Schoenflies uses the letters T (from *Tetraëder*) and O (*Oktaëder*) with the addition in corresponding cases of subscripts h and d, e.g., $T_h=3L^24L_6^33PC$.

SHUBNIKOV NOTATION

Simple axes of symmetry are denoted by figures indicating the degree of the axis, e.g., 4 stands for a fourfold axis. A plane of symmetry is denoted by the letter m (from the French word *miroir*—mirror). Perpendicularity is shown by a colon, while parallelism by a dot. For instance, $m\cdot 3 : m$ means that the basic symmetry elements in this case are a threefold axis and two symmetry planes, one of which is perpendicular and the other parallel to the axis. Thus, $m\cdot 3 : m=L^33L^24P$. A fraction would show that the axes do not intersect at right angles, e.g., $3/2=3L^24L^3$.

ORIENTATION OF CRYSTALS

The selection of the direction of three rows as axes I, II, and III, and of one of the faces as a unit face is called the *orientation of a crystal*. The rules for orientation are given below.

The law of rational indices makes it possible to use very simple and convenient designations for the spatial position of each crystal face. Having selected a definite orientation, we can fix the spatial position of any face with the aid of three numerical parameters. For instance, in the case shown in Fig. 70, we have designations $2a : 3b : 6c$ for the Oa_2, Ob_3, Oc_6 face.

This method was first used by Weiss in 1818. In 1839 W. H. Miller suggested a still more convenient method which is now used almost universally: replacement of Weiss numerical parameters (p, q, r) with their reciprocals $\left(\frac{1}{p}, \frac{1}{q}, \frac{1}{r}\right)$. In the general case three regular fractions will be obtained, and the ratio between them can always be expressed by three whole numbers.

These three figures which must not have a common factor (multiplier) are called *face indices*. They are usually designated by the letters h, k, l or (after Fedorov) p_1, p_2, p_3.

Miller's method is convenient because the indices, i.e., reciprocals of intercepts made by a face on the reference axes and measured in axial units, are directly written into the formula of a plane. For instance, $Ax+By+Cz+D=0$. The free term D is equivalent to zero because any face, in accordance with the law of constancy of angle, can be translated parallel to itself so that it would pass through the origin. In this case it is not the numerical parameters 2 : 3 : 6

that should be taken, but their reciprocals $\frac{1}{2}:\frac{1}{3}:\frac{1}{6}$, i. e., three always regular fractions. Without changing their ratio Miller transforms them into whole numbers: $\frac{1}{2}:\frac{1}{3}:\frac{1}{6}=\frac{6}{2}:\frac{6}{3}:\frac{6}{6}=3:2:1$. The three figures—face indices, enclosed in round brackets, denote the face symbol (321), the ratio sign (:) being usually omitted.

Thus, a *face symbol is a combination of three smallest figures which are inversely proportional to the numerical parameters of the face.*

When a face intersects the negative direction of an axis, a bar is placed over the corresponding index, e.g., $(3\bar{2}1)$, if the face intersects the axis *II* to the left of the origin.

If a face is parallel to one or two axes, its Weiss parameters along these axes will be infinitely large. Insofar as $\frac{1}{\infty}=0$, the 0 index in Millerian symbols implies parallelism between the particular face and the corresponding axis.

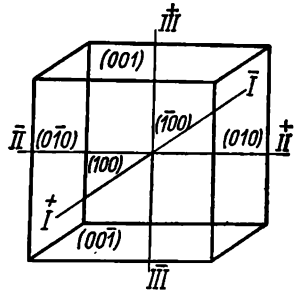


Fig. 74. Symbols of cube faces

Let us review, for example, the symbols denoting the six faces of a cube (Fig. 74). The directions of its three mutually perpendicular edges will serve as axes *I*, *II*, *III*, therefore, $\alpha=\beta=\gamma=90°$.

The unit face in the cubic lattice should coincide with the spatial diagonal plane perpendicular to the threefold axis. Therefore, the axial ratio will be $a=b=c$. Placing the origin of the coordinates in the centre of the cube, we obtain the following symbols for its faces: front face (100), rear face $(\bar{1}00)$, right-hand face (010), left-hand face $(0\bar{1}0)$, top face (001), bottom face $(00\bar{1})$.

ORIENTATION OF CRYSTALS OF DIFFERENT SYSTEMS

It can be seen from the above that the face symbols depend on the orientation of the crystal. Hence, if we select different directions as new axes *I*, *II*, and *III* and take as a unit some other face also crossing the three crystallographic axes, we shall obtain different symbols for all the faces. It is evident then, that there must be definite rules for the selection of reference axes and of a unit face, and that there should be a definite orientation for crystals of a given substance.

The rules for determining the definite orientation of a crystal were laid down by E. S. Fedorov and T. W. Barker; they will be given later (see Ch. VIII). Here we shall give simpler rules, which, although

frequently do not enable one to determine the definite orientation of a crystal, are nevertheless convenient and widely used at the present time.

It is quite natural to select the directions related to the symmetry of a crystal as reference axes. Such directions are: (1) symmetry axes, and (2) normals to symmetry planes. Hence, the lower the symmetry of a crystal, i.e., the fewer symmetry axes and planes, the less opportunity there is for imparting a definite orientation to it. The following two general rules are usually observed in the selection of orientation:

(1) reference axes should be selected so as to give the α, β, and γ angles of 90° or close to it;

(2) a unit face should be selected so as to give intercepts of fairly close values on the *I*, *II*, and *III* axes even though not equal: $a \neq b \neq c$.

If none of the crystal faces intersect all the three crystallographic axes, two faces should be taken which intersect two axes each, e.g., *I*(*X*) and *II*(*Y*), *II*(*Y*) and *III*(*Z*). The first face gives the $a : b$ ratio, and the second the $b : c$ ratio. The faces have symbols (110) and (011) and are called *two-unit faces*. If there is only one such face, a complete axial ratio cannot be determined.

Let us analyse the orientation of a crystal for all systems, and in some cases for individual crystal classes.

Cubic System. All crystal classes in this system have three mutually perpendicular axes—either $3L^4$ or $3L^2$. They can always be used as the *I*, *II*, and *III* axes, no matter which of them is oriented vertically, which from right to left, and which towards the observer, since in rotation about the L^3 axis these axes will exchange places; thus, $\alpha=\beta=\gamma=90°$. The unit face in the cubic system must always give equivalent intercepts on all the three axes, since here $a=b=c$. Such faces are those of a tetrahedron or an octahedron. It is obvious that in the cubic system a unique orientation comes virtually of its own accord.

Tetragonal System. All crystal classes in this system have one axis of a higher degree: L^4 or L_4^2. Besides, most of the crystal classes have twofold axes which are perpendicular to the fourfold axis, and planes of symmetry which intersect this axis. The axis of a higher degree is always selected as the vertical one (*III*), and the two L^2 axes perpendicular to it, as the axes *I* and *II* (Fig. 75). If there are no such axes, they are replaced by normals to two mutually perpendicular planes intersecting along the *III* axis. When there are no such planes (classes L^4, L^4PC, and L_4^2), the directions of two edges which are perpendicular to one another and to the fourfold axis are taken as the axes *I* and *II*, the rule of $\alpha=\beta=\gamma=90°$ being observed.

The unit face no longer retains the unvarying position which it has in the cubic system. Insofar as $a=b\neq c$, the projection of the unit face must lie on the bisectrix of the angle *I-II*, or γ. That face is usually selected whose projection is the closest to the corresponding position of (111) in the cubic system, i.e., to the termination of the L^3 axis. It has already been said that the unit face is a solid diagonal of the parallelepiped of a lattice. Therefore, in those cases in which we can determine the shape and the size of the parallelepiped by X-ray examination, we shall have no doubt as to which is the unit face.

Orthorhombic System. Two of the three crystal classes of the system have three mutually perpendicular twofold axes which are

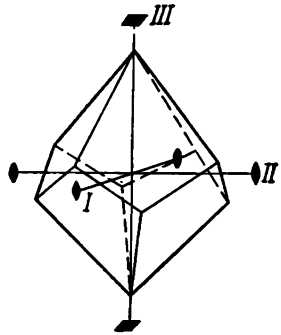


Fig. 75. Orientation for tetragonal crystals

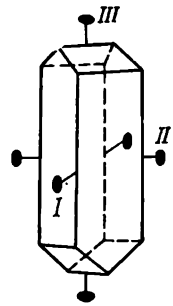


Fig. 76. Orientation for rhombic crystals

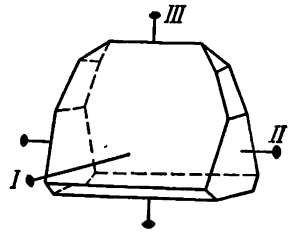


Fig. 77. Orientation for crystals of the $L^2 2P$ class

taken as the axes *I*, *II*, and *III* (Fig. 76). In the third crystal class ($L^2 2P$) the twofold axis is used as the vertical axis *III*, and the normals to $2P$ are the axes *I* and *II*, respectively (Fig. 77). As a unit face is taken that of the oblique faces the projection of which lies closest to the centre of a spherical triangle formed on the projection by termination points of the coordinate axes.

Monoclinic System. The number of symmetry elements which could be used as stable directions is very limited. The crystal classes of this system have only one twofold axis or one symmetry plane *P*. The L^2 axis or the normal to *P* is always chosen as the horizontal axis *II*. The directions of the edges of two zones are to be used as the other two coordinate axes. These directions are so chosen that they fulfil the condition $\alpha=\gamma=90°$; $\beta\neq 90°$.

Terminations in the direction parallel to the zone edges are found on a projection in the poles of the great circle containing the poles of the faces of that zone. Axis *III* is always vertical, therefore, its

positive termination must be in the centre of the primitive circle of the projection. Axis *I* should terminate in the intermediate great circle, i.e., on the vertical diameter of the primitive circle at a point removed from the centre by an angle that is never quite 90° but fairly close to it. Two cases may arise here:

(1) When $\beta > 90°$, the positive end of the axis *I* emerges in the lower part of the sphere, i.e., below the projection plane. In the upper part we find a diametrically opposite point, i.e., the termination of the negative end which is at an angle of $180° - \beta$ to the axis *III* (Fig. 78, *a*).

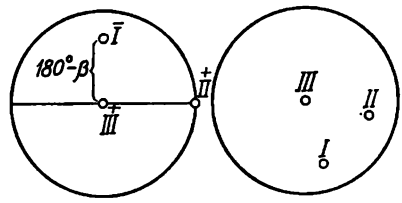


Fig. 78. Orientation of crystals:
(*a*) of the monoclinic system ($\beta > 90°$); (*b*) of the triclinic system

(2) If $\beta < 90°$, the positive end of the axis *I* will be in the upper hemisphere, and the negative end—in the lower.

That face is selected as a unit face whose pole is closest to the centre of the spherical triangle *I-II-III*.

The reader should bear in mind that in some books and treatises on mineralogy the rule that the angles α, β, γ should be taken between terminations of crystallographic axes with the same sign is not always observed. Thus, the angle β in the monoclinic system is often taken not between $\overset{+}{X}$ and $\overset{+}{Y}$, but between $\overset{-}{X}$ and $\overset{-}{Y}$. In such cases the correct angle β will be obtained if the value of the angle given is subtracted from 180°.

Triclinic System. This system has no elements of symmetry which would give a stable direction (classes L^1 and *C*). The directions of the edges of the three zones have to be taken as reference axes, provided that the oblique angles α, β, and γ, although unequal, are as close to right angles as possible.

Axis *III* is always projected in the centre, because its corresponding (vertical) zone coincides with the primitive circle of the projection. If α, β, and γ are less than 90°, the positive ends of the axes *I* and *II* emerge in the lower and right-hand parts, respectively, of the primitive circle plane (Fig. 78, *b*). When α and β are greater

than 90°, the diametrically opposed terminations of the negative ends of the respective axes have to be used.

Trigonal and hexagonal systems are unique as regards orientation. In these systems four directions are used for crystallographic axes instead of three. The reason for this is that in orienting a crystal with respect to the three axes the faces of the same simple form may be given indices that have not only different signs and place in the formula, but even different figures, which is highly inconvenient. In these systems $a=b\neq c$ and $\alpha=\beta=90°$; $\gamma=120°$.

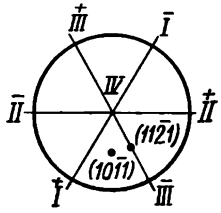


Fig. 79. Orientation for hexagonal crystals

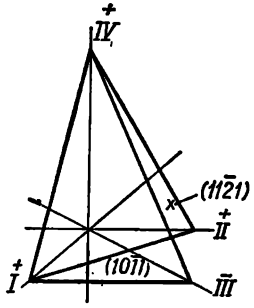


Fig. 80. Possible unit faces in the hexagonal system

The vertical axis, designated here by the figure *IV* or the letter *Z*, is always the only axis of a higher degree in each case. The other three axes, designated by the Roman numerals *I*, *II*, *III* or by the letters *X*, *Y*, and *U*, are three twofold axes. Should there be no such axes, use is made of normals to vertical symmetry planes or of the corresponding directions of the three edges. The arrangement of the axes is shown in Figs. 79 and 80. The axis *II* always extends from right to left. The axes *I* and *III* are directed towards the observer: the axis *I* to the left, and the axis *III* to the right. The positive and negative directions alternate (see Fig. 79), so that the terminations of the axes which are adjacent in the primitive circle have different signs.

In orientation for four axes the unit face has a symbol differing from the usual (111). Insofar as in the trigonal and hexagonal systems $a=b\neq c$, $\alpha=\beta=90°$, and $\gamma=120°$, and the axes *I*, *II* and *III* are located in the same plane, the unit face obviously cannot intersect all these three axes at the same distance from the origin. It can give equal intercepts either on two adjacent axes, e.g., on the axes *I* and *III*, or on two non-adjacent axes, such as *I* and *II* (see Fig. 80). In the first case the unit face is parallel to the third horizontal axis, *II*, and will have the symbol (10$\bar{1}$1); in the second case

it intersects the third axis *III* at half the distance, i.e., its symbol is $(11\bar{2}1)$.

A very important rule for this orientation is that the *sum of indices on the horizontal axes is always zero, i.e.*, $p_1+p_2+p_3=0$. We arrive at this rule in the following manner.

Fig. 81 shows a plane wherein are located three crystallographic axes: *I*(*X*), *II*(*Y*), and *III*(*U*). The positive and negative directions of the axes are marked accordingly. The axis *IV*(*Z*) is perpendicular to the plane of the diagram and terminates at the point *O*. A face *MM'*

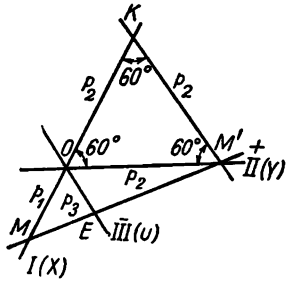


Fig. 81. A drawing to the theorem concerning the sum of indices

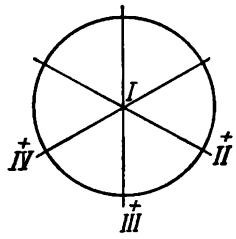


Fig. 82. Orientation for hexagonal crystals according to Fedorov

intersects all the three horizontal axes. It may be parallel to the axis *IV*(*Z*) or inclined towards it. Let us draw a line *M'K* parallel to the axis *III*(*U*) and designate the intercepts made by the face *MM'* on the three horizontal axes by the letters p_1, p_2, p_3. The triangle *OM'K* is equilateral, so that each of its three angles is 60°. It can be seen from the drawing that

$$\frac{p_1+p_2}{p_2}=\frac{p_1}{p_3}.$$

We divide both sides of the equation by p_1:

$$\frac{p_1+p_2}{p_1\cdot p_2}=\frac{1}{p_3}.$$

Hence

$$\frac{p_1}{p_1\cdot p_2}+\frac{p_2}{p_1\cdot p_2}=\frac{1}{p_3}.$$

Cancelling, we obtain

$$\frac{1}{p_2}+\frac{1}{p_1}=\frac{1}{p_3}.$$

Insofar as indices are reciprocals of numerical parameters, we obtain

$$i+h=k,$$

where

$$h=\frac{1}{p_1},$$

$$i=\frac{1}{p_2}$$

and

$$k=\frac{1}{p_3}$$

or

$$h+i-k=0*.$$

As k is an index in the negative direction of the axis $III(U)$, it should have the minus sign, so when it is transferred to the left-hand side of the equation, we obtain

$$h+i+k=0.$$

The orientation that we have used is called the *Bravais orientation*. There are other orientations, of which we shall mention the following.

1. *Fedorov's Orientation.* The number of axes is the same as in the Bravais orientation, but their arrangement and signs are different. The first axis (I) is vertical, the third ($\overset{+}{III}$) is directed towards the observer. At an angle of 60° to the right of it is the second axis ($\overset{+}{II}$), and to the left the fourth axis ($\overset{+}{IV}$) (Fig. 82).

2. *Miller's Orientation.* This orientation makes use of three reference axes instead of four. The directions of the axes are those of the edges of intersection of three faces which are equally inclined to the axis of the higher degree (Fig. 83). In this case the relation between the constants is different from that shown in Table 3, being $a=b=c$, $\alpha=\beta=\gamma\neq 90°$. The unit face also occupies a different position. Insofar as all the interaxial angles here are equal, it is enough to know one of them which is denoted by the letter α.

Some authors use the Miller orientation for the trigonal system, which is sometimes called rhombohedral (see page 73). Its trinomial symbols are related to the quadrinomial ones as follows.

If $(hikl)$ is a face symbol in the Bravais orientation, and (pqr) is the symbol of the same face in the Miller orientation, then

$$p:q:r=(h-k+l):(i-h+l):(k-i+l)$$

and

$$h:i:k:l=(p-q):(q-r):(r-p):(p+q+r).$$

* This proof, the simplest of all those suggested, has been given by Academician N. V. Belov.

Miller's is the most convenient method of designation of faces and edges of crystals by symbols consisting of three or four indices.

But in some works on crystallography and mineralogy other methods of designation are used. The following comparative tables are used in changing from one system of designations to another.

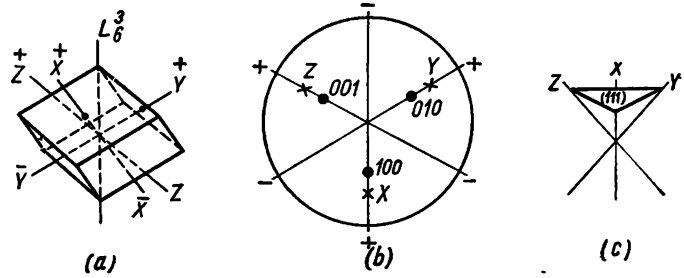


Fig. 83. Orientation for hexagonal crystals according to Miller:
(*a*) position of axes in space; (*b*) position of axes on a projection; (*c*) position of a unit face

The author has deemed it sufficient to give tables for the cubic and hexagonal systems. Below is the explanation of the origin and meaning of the different methods of designation.

In A. Lévy's designations the original idea belonged to Haüy; Lévy and Des Cloizeaux only improved and perfected his method.

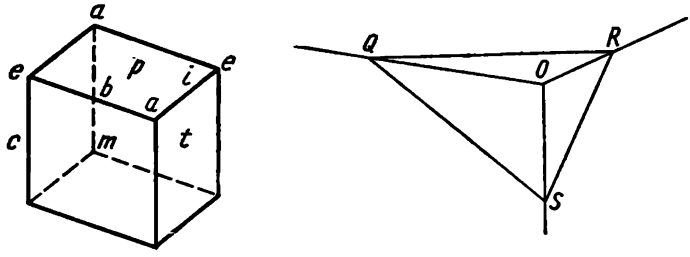


Fig. 84. Designation of faces, angles, and edges according to Haüy

The principal elementary parallelepiped of any lattice is bounded by three pairs of faces. These are denoted by three consonants from the word *primitif* (initial)—*p*, *m*, *t*. The four angles are denoted by vowels—*a*, *e*, *i*, *o*, the six edges—by consonants *b*, *c*, *d*, *f*, *q*, *h* (Fig. 84). In denoting faces of various simple forms of the cubic system, the following method is used. The directions of three mutually perpendicular edges (*b*) of a cube are used as reference axes *X*, *Y*, *Z*. A face *QRS* makes three unequal intercepts—*OQ*, *OR*, *OS*—along the axes.

They are designated $\frac{1}{q}$, $\frac{1}{r}$, $\frac{1}{s}$. If, for instance, we have a hexoctahedron {125}, we shall designate it by the Lévy method as b^1, $b^{1/2}$, $b^{1/3}$.

Weiss designated faces with the aid of numerical parameters (see Tables 4 and 5). If the basic form (unit face) is expressed as $(a : b : c)$, any other face will be designated as $(a : nb : mc)$ or $(na : b : mc)$, where m and n are numerical parameters. G. Rose suggested writing the Weiss symbols so as to express the factors, by which the intercepts of the basic form are multiplied, in fractions with 1 as the numerator, e.g.,

$$\left(\frac{1}{mn}a : \frac{1}{m}b : \frac{1}{n}c\right)$$

or

$$\left(\frac{1}{m}a : \frac{1}{mn}b : \frac{1}{n}c\right).$$

The method suggested by K. F. Naumann designates the basic form by the letter P (pyramid), and in the cubic system by the letter O (octahedron). The above-mentioned factors m and n are added to these letters if the factors are not equal to unity, e.g., mOn, mPn, ∞On. These designations apply solely to forms of that crystal class in a system which has the highest symmetry (so-called *holohedry*). In designating forms of classes with lower symmetry (so-called *hemihedral*, *tetrahedral* and *hemimorphic* classes) Naumann used the symbols $\frac{mOn}{2}$ or $\frac{mOn}{4}$ with different signs showing the class of symmetry of the forms.

V. M. Goldschmidt's symbols radically differ from those of other authors. Goldschmidt's symbols consist of two, sometimes even of one figure, instead of the usual three parameters of Weissian or Millerian indices. In essence his method of designation is this.

All the three indices of the Millerian symbol can be divided by the value of the third index, i.e., one relating to the vertical axis Z. Three fractions are thus obtained, the last of which is always unity and, therefore, is not written.

The two remaining fractions (on the X and Y axes) comprise Goldschmidt's symbol. If these fractions are equal, only one of them is written.

The following are examples of conversion from Millerian to Goldschmidt's symbols.

1. Millerian symbol (233) $\longrightarrow \frac{2}{3} : \frac{3}{3} : \frac{3}{3} \longrightarrow \frac{2}{3}1$.

2. Millerian symbol (112) $\longrightarrow \frac{1}{2} : \frac{1}{2} : 1 \longrightarrow \frac{1}{2}$.

System and its geometrical constants	Formula of crystal class	Orientation
Cubic $a=b=c$ $\alpha=\beta=\gamma=90°$ All constants are known	$3L^4 4L^3_6 6L^2 PC$ $3L^4 4L^3 6L^2$	X, Y, and $Z-3L^4$
	$3L^2_4 4L^3 6P$	X, Y, and $Z-3L^2_4$
	$3L^2 4L^3_6 3PC$ $3L^2 4L^3$	X, Y, and $Z-3L^2$
Tetragonal $a=b\neq c$ $\alpha=\beta=\gamma=90°$ One constant must be calculated: $a:c$	$L^4 4L^2 5PC$ $L^4 4L^2$	$Z-L^4$, X and $Y-2L^2$
	$L^4 4P$	$X-L^4$, X and Y—perpendiculars to $2P$
	$L^4 PC$ L^4	$Z-L^4$, X and Y—directions of two edges perpendicular to L^4
	$L^2_4 2L^2 2P$	$Z-L^2_4$, X and $Y-2L^2$
	L^2_4	$Z-L^2_4$, X and Y—directions of two edges perpendicular to L^2_4
Orthorhombic $a\neq b\neq c$ $\alpha=\beta=\gamma=90°$ Two constants must be calculated: $a:b:c$	$3L^2 3PC$ $3L^2$	X, Y, and $Z-3L^2$
	$L^2 2P$	$Z-L^2$, X and Y—perpendiculars to $2P$

* The hexagonal and trigonal systems are oriented with respect to 4 axes, the order

Table 3

crystals

System and its geometrical constants	Formula of crystal class	Orientation
Monoclinic $a \neq b \neq c$ $\alpha = \gamma = 90°$; $\beta \neq 90°$ Three constants must be calculated: $a:b:c$, angle β	L^2PC L^2	Y—L^2, X and Z—directions of two edges perpendicular to L^2
	P	Y—perpendicular to P; X and Z—directions of two edges perpendicular to Y
Triclinic $a \neq b \neq c$ $\alpha \neq \beta \neq \gamma \neq 90°$ Five constants must be calculated: $a:b:c$, angles: α, β, γ	C L^1	X, Y, and Z—directions of edges of three zones
Hexagonal * $a = b \neq c$ $\alpha = \beta = 90°$; $\gamma = 120°$ One constant must be calculated: $a:c$	L^66L^27PC; L^66L^2	Z—L^6, X, Y, and U—$3L^2$
	L^66P	Z—L^6, X, Y, and U—perpendiculars to $3P$
	L^6PC L^6	Z—L^6, X, Y, and Z—directions of three edges perpendicular to L^6
	L^33L^24P	Z—L^3, X, Y, U—$3L^2$
	L^3P	Z—L^3, X, Y, and U—directions of three edges perpendicular to L^3
Trigonal $a = b \neq c$ $\alpha = \beta = 90°$; $\gamma = 120°$ One constant must be calculated: $a:c$ or angle α in Miller orientation	$L_6^33L^23PC$ L^33L^2	Z—L_6^3, Z—L^3: X, Y, and U—$3L^2$
	L^33P	Z—L^3, X, Y, and U are perpendicular to $3P$ or parallel to $3P$ and perpendicular to L^3
	L_6^3C L^3	Z—L_6^3 or L^3, X, Y, and U—directions of three edges perpendicular to L_6^3 or L^3

of indices being as follows: 1st, 2nd, and 3rd are on X, Y, and U, 4th on Z.

Table 4

Designations of simple forms of the hexoctahedral crystal class of the cubic system according to different authors

Form	Miller	A. Lévy	Naumann	Weiss-Rose		Goldschmidt	Note
Cube	$\{100\}$	P	$\infty\,0\,\infty$	$a:\infty a:\infty a$	a	0	
Octahedron	$\{111\}$	a^1	0	$a:a:a$	0	1	
Rhombic dodecahedron	$\{110\}$	b^1	$\infty\,0$	$a:a:\infty a$	d	∞	
Tetrahexahedron	$\{qro\}$	$b^{\frac{q}{r}}$	$\infty\,0^{\frac{q}{r}}$	$a:\frac{r}{q}a:\infty a$	$\frac{r}{q}d$		$q>r$*
	$\{320\}$	$b^{\frac{3}{2}}$	$\infty\,0^{\frac{3}{2}}$	$a:\frac{2}{3}a:\infty a$	$\frac{2}{3}d$	$\infty\,\frac{2}{3}$	
	$\{310\}$	b^3	$\infty\,03$	$a:\frac{1}{3}a:\infty a$	$\frac{1}{3}d$	$3\,\infty$	
	$\{210\}$	b^2	$\infty\,02$	$a:\frac{1}{2}a:\infty a$	$\frac{1}{2}d$	$2\,\infty$	
Tetragonal trioctahedron	$\{qrr\}$	$a^{\frac{q}{r}}$	$\frac{q}{r}\,0\,\frac{q}{r}$	$a:a:\frac{r}{q}a$	$\frac{r}{q}\,0$	$\frac{q}{r}\,1$	$q>r$*
	$\{322\}$	$a^{\frac{3}{2}}$	$\frac{3}{2}\,0\,\frac{3}{2}$	$a:a:\frac{2}{3}a$	$\frac{2}{3}\,0$	$\frac{3}{2}\,1$	
	$\{311\}$	a^3	303	$a:a:\frac{1}{3}a$	$\frac{1}{3}\,0$	31	
	$\{211\}$	a^2	202	$a:a:\frac{1}{2}a$	$\frac{1}{2}\,0$	21	
Trigonal trioctahedron	$\{qqr\}$	$a^{\frac{r}{q}}$	$\frac{q}{r}\,0$	$a:\frac{r}{q}a:\frac{r}{q}a$	$\frac{q}{r}\,0$	$\frac{q}{r}$	$q>r$*
	$\{332\}$	$a^{\frac{2}{3}}$	$\frac{3}{2}\,0$	$a:\frac{2}{3}a:\frac{2}{3}a$	$\frac{3}{2}\,0$	$\frac{3}{2}$	
	$\{331\}$	$a^{\frac{1}{3}}$	30	$a:\frac{1}{3}a:\frac{1}{3}a$	30	3	
	$\{221\}$	$a^{\frac{1}{2}}$	20	$a:\frac{1}{2}a:\frac{1}{2}a$	20	2	
Hexoctahedron	$\{qrs\}$	$b^{\frac{1}{s}}\ b^{\frac{1}{r}}\ b^{\frac{1}{q}}$	$\frac{q}{s}\,0\,\frac{q}{r}$	$a:\frac{s}{r}a:\frac{s}{q}a$		$\frac{q}{s}\,\frac{r}{s}$	$q>r>s$*

* Inequalities are in Millerian symbols (first column).

Table 4 (continued)

Form	Miller	A. Lévy	Naumann	Weiss-Rose	Goldschmidt	Note
Hexoctahedron	$\{432\}$	$b^{\frac{1}{2}}\ b^{\frac{1}{3}}\ b^{\frac{1}{4}}$	$20\frac{4}{3}$	$a:\frac{2}{3}a:\frac{1}{2}a$	$2\frac{3}{2}$	
	$\{431\}$	$b^{1}\ b^{\frac{1}{3}}\ b^{\frac{1}{4}}$	$40\frac{4}{3}$	$a:\frac{1}{3}a:\frac{1}{4}a$	43	
	$\{421\}$	$b^{1}\ b^{\frac{1}{2}}\ b^{\frac{1}{4}}$	402	$a:\frac{1}{2}a:\frac{1}{4}a$	42	
	$\{321\}$	$b^{1}\ b^{\frac{1}{2}}\ b^{\frac{1}{3}}$	$30\frac{3}{2}$	$a:\frac{1}{2}a:\frac{1}{3}a$	32	

Table 5

Designations of simple forms of the dihexagonal bipyramidal crystal class of the hexagonal system according to different authors *

Form	Bravais	A. Lévy	Naumann	Weiss-Rose		Goldschmidt
Pinacoid	$\{0001\}$	p	$0P$	$\infty a:\infty a:\infty a:c$	c	0
Hexagonal prism of II order	$\{10\bar{1}0\}$	m	∞P	$a:a:\infty a:\infty c$	g	$\infty 0$
Hexagonal prism of I order	$\{11\bar{2}0\}$	hL^{1}	$\infty P2$	$2a:a:2a:\infty c$	a	∞
Dihexagonal prism	$\{qri0\}$	$h^{\frac{q}{r}}$	$\infty P\frac{i}{q}$	$a:\frac{r}{i}a:\frac{r}{q}a:\infty c$	$\frac{r}{i}q$	
	$\{21\bar{3}0\}$	h^{2}	$\infty P\frac{3}{2}$	$a:\frac{1}{3}a:\frac{1}{2}a:\infty c$	$\frac{1}{3}g$	2∞
	$\{31\bar{4}0\}$	h^{3}	$\infty P\frac{4}{3}$	$a:\frac{1}{4}a:\frac{1}{3}a:\infty c$	$\frac{1}{4}g$	3∞
	$\{32\bar{5}0\}$	$h^{\frac{2}{3}}$	$\infty P\frac{5}{3}$	$a:\frac{2}{5}a:\frac{2}{3}a:\infty c$	$\frac{2}{5}g$	$\frac{3}{2}\infty$
Hexagonal bipyramid of II order	$\{q0\bar{q}s\}$	$b^{\frac{s}{q}}$	$\frac{q}{s}P$	$a:a:\infty a:\frac{q}{s}c$	$\frac{q}{s}r$	

* Millerian symbols are not listed, since he gives a 3-axis orientation for hexagonal crystals.

Table 5 (continued)

Form	Bravais	A. Lévy	Naumann	Weiss-Rose		Gold-schmidt
Hexagonal bipyramid of II order	$\{10\bar{1}1\}$	b^1	P	$a:a:\infty\, a:c$	r	10
	$\{10\bar{1}2\}$	$b^{\frac{1}{2}}$	$\frac{1}{2}P$	$a:a:\infty\, a:\frac{1}{2}c$	$\frac{1}{2}r$	$\frac{1}{2}0$
	$\{20\bar{2}1\}$	$b^{\frac{1}{2}}$	$2P$	$a:a:\infty\, a:2c$	$2r$	20
Hexagonal bipyramid of I order	$\{qq\bar{2}qs\}$	$a^{\frac{s}{q}}$	$\frac{2q}{s}P2$	$2a:a:2a:\frac{2q}{s}c$	$\frac{2}{s}qd$	
	$\{11\bar{2}1\}$	a^1	$2P2$	$2a:a:2a:2c$	$2d$	1
	$\{11\bar{2}2\}$	a^2	$P2$	$2a:a:2a:c$	d	$\frac{1}{2}$
	$\{22\bar{4}1\}$	$a^{\frac{1}{2}}$	$4P2$	$2a:a:2a:4c$	$4d$	42
Dihexagonal bipyramid	$\{pr\bar{i}s\}$	$b^{\frac{1}{r}}\, b^{\frac{1}{q}}\, h^{\frac{1}{s}}$	$\frac{i}{s}P\frac{i}{q}$	$a:\frac{r}{i}a:\frac{r}{q}a:\frac{r}{s}c$	—	
	$\{21\bar{3}3\}$	$b^1\, b^{\frac{1}{2}}\, h^{\frac{1}{3}}$	$P\frac{3}{2}$	$a:\frac{1}{3}a:\frac{1}{2}a:\frac{1}{3}c$	—	$\frac{2}{3}\frac{1}{3}$
	$\{21\bar{3}2\}$	$a^{\frac{1}{2}}$	$\frac{3}{r}P\frac{3}{r}$	$a:\frac{1}{3}a:\frac{1}{2}a:\frac{1}{2}c$	—	$1\frac{1}{2}$
	$\{21\bar{3}1\}$	a_2	$3P\frac{3}{2}$	$a:\frac{1}{3}a:\frac{1}{2}a:c$	—	21
	$\{31\bar{4}3\}$	$a^{\frac{1}{3}}$	$\frac{4}{3}P\frac{4}{3}$	$a:\frac{1}{4}a:\frac{1}{3}a:\frac{1}{3}c$	—	$1\frac{1}{3}$
	$\{21\bar{4}2\}$	$b^1\, b^{\frac{1}{3}}\, h^{\frac{1}{2}}$	$2P\frac{4}{3}$	$a:\frac{1}{4}a:\frac{1}{3}a:\frac{1}{2}c$	—	$\frac{3}{2}\frac{1}{2}$
	$\{31\bar{4}1\}$	a_3	$4P\frac{4}{3}$	$a:\frac{1}{4}a:\frac{1}{3}a:c$	—	31
	$\{32\bar{5}3\}$	$a^{\frac{2}{3}}$	$\frac{5}{3}P\frac{5}{3}$	$a:\frac{2}{5}a:\frac{2}{3}a:\frac{2}{3}c$	—	$1\frac{2}{3}$
	$\{32\bar{5}2\}$	$a^{\frac{3}{2}}$	$\frac{5}{2}P\frac{5}{3}$	$a:\frac{2}{5}a:\frac{2}{3}a:c$	—	$\frac{3}{2}1$
	$\{32\bar{5}1\}$	$b^{\frac{1}{2}}\, b^{\frac{1}{3}}\, L^1$	$5P\frac{5}{3}$	$a:\frac{2}{5}a:\frac{2}{3}a:2c$	—	32

The conversion operation from Goldschmidt's symbols to Millerian ones produces:

1. Goldschmidt's symbol $\frac{2}{3}1 \longrightarrow \frac{2}{3}:1:1$ is multiplied by three, yielding $\frac{2\cdot 3}{3}:3:3=(233)$—Millerian symbol.

2. Goldschmidt's symbol $\frac{1}{2} \longrightarrow \frac{1}{2}:\frac{1}{2}:1$ is multiplied by two, yielding $\frac{2}{2}:\frac{2}{2}:2=(112)$ Millerian symbol.

Goldschmidt's method results not in simplification but in complication of very simple and clear Millerian symbols.

CHAPTER VII

Zone Law. Relationship Between Symbols of Faces and Edges

It was said in Chapter I that a *zone is a complement of faces intersecting along parallel edges. The direction of these edges translated parallel to themselves up to the origin of coordinates is the zone axis.* On a stereographic projection the poles of all the faces of a zone are located on one great circle, the zone axis terminating at the poles of this circle.

A zone is *primary* or *complete* if all the faces in it intersect and produce real edges. A zone is *secondary* or *incomplete* if some of its faces intersect, when produced, along edges which are actually nonexistent in the crystal, but which could have existed had the faces developed differently.

Taking the space lattice as the basis of crystal structure we can make the following deductions:

(a) any line passing through any two nodes of a lattice is the direction of a crystal edge, and

(b) any plane passing through any three nodes of different rows is a possible crystal face.

The following two postulates are known in crystallography as the *zone law.*

1. *Any plane parallel to two real or possible crystal edges is a real or possible crystal face.*

2. *Any direction parallel to the line of intersection of two real or possible crystal faces is always a real or possible crystal edge.*

The direction of an edge in the orientation adopted for a particular crystal is also designated by three or four (in the hexagonal system) whole numbers, which are called *edge indices.* We shall designate them by the letters r_1, r_2, r_3.

Any edge can be translated parallel to itself so as to pass through the origin. The coordinates of any node on the edge will fix its direction unambiguously. The *edge symbol* will thus consist of three indices enclosed in square brackets. Having cancelled out the common multipliers or having taken the indices of that node of the row which

is nearest the origin, we obtain the edge symbol. The difference between edge indices and face indices is that the former are not reciprocals of numerical parameters but are equivalent to them.

Figure 85 shows the construction of an edge with the symbol [123]. Three rows *MK*, *MF*, *MR* parallel to crystallographic axes are drawn from node *M* (the first node from the origin). Intersecting coordinate planes *I-III*, *I-II*, and *II-III*, the rows define the plane nets, and the positions of points can be given as whole numbers of intercepts of the corresponding rows. Thus, the row *OM* (Fig. 85) is defined by the symbol [123].

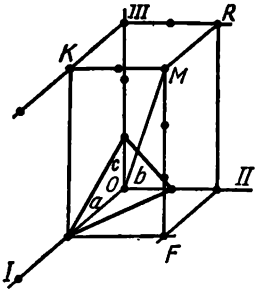


Fig. 85. Derivation of an edge symbol

In a general form, adopting the coordinates of any node on an edge as *X*, *Y*, *Z* and measuring them by the intercepts of the rows taken as the directions of reference axes *I*, *II*, *III*, we obtain

$$r_1 : r_2 : r_3 = \frac{X}{a} : \frac{Y}{b} : \frac{Z}{c}.$$

In our instance

$$r_1 : r_2 : r_3 = \frac{MR}{a} : \frac{MK}{b} : \frac{MF}{c} = 1 : 2 : 3.$$

The symbols of all parallel edges are identical: they are the symbols of the axes of the corresponding zones. It should be noted that the position of the same edge can be expressed by two symbols consisting of the same indices in the same order but with opposite signs. For instance,

$$[123] = [\bar{1}\bar{2}\bar{3}] \text{ or } [110] = [\bar{1}\bar{1}0].$$

The crystallographic axes have the following symbols:

$$I\text{—}[100],\ II\text{—}[010],\ III\text{—}[001].$$

The relationship between face and edge symbols is described by:

$$p_1 r_1 + p_2 r_2 + p_3 r_3 = 0. \qquad (1)$$

This can be proved in the following way.

We can always make an edge pass through the origin by parallel translation. Let us take an arbitrary point *M* (see Fig. 85) on the edge *OM*. Its coordinates are X_0, Y_0, and Z_0. The unit face gives intercepts *a*, *b*, *c* on the corresponding axes; then

$$\frac{X_0}{a} : \frac{Y_0}{b} : \frac{Z_0}{c} = r_1 : r_2 : r_3. \qquad (2)$$

The equation of a plane passing through the origin and parallel to the unit face is

$$\frac{X}{a'}+\frac{Y}{b'}+\frac{Z}{c'}=0, \tag{3}$$

where a', b', and c' are intercepts produced by the given face on the coordinate axes.

The equation of the line parallel to the given edge and passing through the origin is

$$\frac{X}{X_0}=\frac{Y}{Y_0}=\frac{Z}{Z_0}. \tag{4}$$

If a given edge lies in a given face, the given line is in a parallel plane, and the coordinates of its points should satisfy the equation of a plane, i. e.,

$$\frac{X_0}{a'}+\frac{Y_0}{b'}+\frac{Z_0}{c'}=0. \tag{5}$$

We shall express the coordinates X_0, Y_0, and Z_0 in terms of edge symbols, and the intercepts a', b', and c' in terms of face symbols. From the equation (2) we have:

$$r_1=m\frac{X_0}{a};\quad r_2=m\frac{Y_0}{b};\quad r_3=m\frac{Z_0}{c}$$

or

$$X_0=\frac{ar_1}{m};\quad Y_0=\frac{br_2}{m};\quad Z_0=\frac{cr_3}{m},$$

where m is the coefficient of proportionality.

For the face symbol we have:

$$\frac{a}{a'}:\frac{b}{b'}:\frac{c}{c'}=p_1:p_2:p_3.$$

Repeating the derivation for the edge, we obtain:

$$p_1=n\frac{a}{a'};\quad p_2=n\frac{b}{b'};\quad p_3=n\frac{c}{c'}$$

or

$$a'=n\frac{a}{p_1};\quad b'=n\frac{b}{p_2};\quad c'=n\frac{c}{p_3}.$$

Substituting the obtained values of X_0, Y_0, Z_0, and a', b', c' into the equation (5), we get:

$$\frac{ar_1p_1}{mna}+\frac{br_2p_2}{mnb}+\frac{cr_3p_3}{mnc}=0.$$

On cancelling this equation will appear thus:

$$p_1r_1+p_2r_2+p_3r_3=0. \tag{6}$$

This formula expresses the relationship between the indices of the face and the edge lying in it. The formula facilitates the solution of problems often encountered in practical crystallography. Here are a few instances.

1. Determine a characteristic feature of the face symbols of a definite zone. From the definition of the zone we know that all its edges are parallel, i.e., have the same symbol. Therefore, when translated to the origin, the edges give one direction, which is the zone axis and also has the same symbol. Let us take the zone [111]. Substituting the values of r_1, r_2, and r_3 into the equation (6), we obtain:

$$p_1 \cdot 1 + p_2 \cdot 1 + p_3 \cdot 1 = 0.$$

Hence

$$p_1 + p_2 + p_3 = 0.$$

This means that all the faces with the sum of indices equivalent to zero belong to the zone [111].

For the zone [001] we have:

$$p_1 \cdot 0 + p_2 \cdot 0 + p_3 \cdot 1 = 0,$$

hence,

$$p_3 = 0.$$

Consequently, all the faces with the third index equivalent to zero belong to the zone [001].

2. Given the symbols of two faces, it is necessary to determine the symbol of the direction (edge) of their intersection. Two faces $(p_1p_2p_3)$ and $(m_1m_2m_3)$ intersect, i.e., have a common edge. Determine the symbol of this edge $[r_1r_2r_3]$.

Insofar as the faces have a common edge, we can write the following equations:

$$p_1r_1 + p_2r_2 + p_3r_3 = 0,$$
$$m_1r_1 + m_2r_2 + m_3r_3 = 0.$$

Having solved these equations, we obtain:

$$r_1 : r_2 : r_3 = (p_2m_3 - p_3m_2) : (p_3m_1 - p_1m_3) : (p_1m_2 - p_2m_1).$$

The binomials of the right-hand side of the equation are the determinants

$$\begin{vmatrix} p_2 & p_3 \\ m_2 & m_3 \end{vmatrix}, \quad \begin{vmatrix} p_3 & p_1 \\ m_3 & m_1 \end{vmatrix}, \quad \begin{vmatrix} p_1 & p_2 \\ m_1 & m_2 \end{vmatrix},$$

which are obtained from the matrix

$$\begin{Vmatrix} p_1 & p_2 & p_3 \\ m_1 & m_2 & m_3 \end{Vmatrix}$$

by the following method:

$$\begin{array}{c|cccccc|c} p_1 & p_2 & & p_3 & & p_1 & p_2 & p_3 \\ & & \times & & \times & & & \\ m_1 & m_2 & & m_3 & & m_1 & m_2 & m_3 \end{array}$$

There is a rule for this which is easy to memorize. To obtain the symbol for the edge of intersection of two faces, do as follows:

(1) write down the indices of each face symbol twice, in two lines, one under the other;

(2) strike off the extreme right- and left-hand columns;

(3) carry out cross-multiplication and take the differences of the products.

This rule can evidently be used for solving the reverse problem—determining a face from the symbols of two edges lying in it. Let us consider two examples.

Example 1. We have faces (320) and (110). Determine the symbol of the edge at their intersection. Solution:

$$\begin{array}{c|cccccc|c} 3 & 2 & & 0 & & 3 & 2 & 0 \\ & & \times & & \times & & & \\ 1 & 1 & & 0 & & 1 & 1 & 0 \end{array};$$

$$r_1 = 0-0=0; \quad r_2 = 0-0=0; \quad r_3 = 3-2=1.$$

The symbol sought is [001].

Example 2. We have two edges: [$\bar{1}$20] and [122]. Determine the symbol of the face bounded by these edges. Solution:

$$\begin{array}{c|cccccc|c} \bar{1} & 2 & & 0 & & \bar{1} & 2 & 0 \\ & & \times & & \times & & & \\ 1 & 2 & & 2 & & 1 & 2 & 2 \end{array};$$

$$p_1 = 4-0=4; \quad p_2 = 0-\bar{2}=2; \quad p_3 = \bar{2}-2=\bar{4};$$

$$p_1 : p_2 : p_3 = 4:2:\bar{4}.$$

After cancelling by 2 the face symbol is found to be [21$\bar{2}$].

Another important rule is the following.

When two faces ($p_1p_2p_3$) and ($m_1m_2m_3$) are tautozonal, r_1, r_2, r_3 of the equation (1) will naturally be identical for these faces. Therefore,

$$p_1r_1 + p_2r_2 + p_3r_3 = 0,$$
$$m_1r_1 + m_2r_2 + m_3r_3 = 0.$$

Adding the two equations, we have:

$$(p_1+m_1)\,r_1 + (p_2+m_2)\,r_2 + (p_3+m_3)\,r_3 = 0,$$

where (p_1+m_1), (p_2+m_2), and (p_3+m_3) are the indices of a new face in the same zone $[r_1r_2r_3]$.

This rule can be formulated as follows: the *summation of the indices of two faces produces the symbol of a new face of a zone whose axis is the direction of the edge at which the two faces intersect.*

Thus it is possible to construct all the possible faces of a crystal of a given substance from a few known faces of this crystal and to determine their symbols. Such construction is called the *development of the complement of faces by periods.*

The construction and calculation can be made most conveniently when there are four faces of the basic tetrahedron, i.e., one in which three faces are coordinate planes (100), (010), and (001), and the fourth is the unit face (111).

Let us discuss the development of a complement for the cubic system (Fig. 86).

The basic faces (100), (010), (001), and (111) are given in projection. The planes defined by the first three faces are coordinate planes, and the directions of the edges at which the planes intersect are coordinate axes. For instance, the edges [100] and [001] produce a coordinate plane *I-III*, and the edge at which the faces (100) and (001) intersect is the direction of the axis *II*.

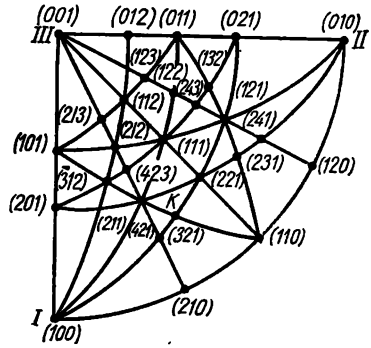


Fig. 86. Development of a complement of faces on a projection

Each zone can be defined by two faces. Consequently, having the four faces mentioned, we can define zones:

(100)—(001), *i. e.*, [010]; (010)—(001), *i. e.*, [100];
(100)—(010), *i. e.*, [001]; (100)—(111), *i. e.*, [0$\bar{1}$1], etc.

At the points of intersection of these zones lie the projections of new faces, whose symbols can be determined by the rule of summation of indices:

$$+\begin{matrix}001\\010\\\hline 011\end{matrix} + \begin{matrix}001\\100\\\hline 101\end{matrix} + \begin{matrix}100\\010\\\hline 110\end{matrix}.$$

These are the faces of the first period. By drawing zones across the initial faces and the faces of the first period, we obtain the faces of the second period: (211), (121), (112); in the same way we obtain the complement of all the possible faces of the crystal.

In summing the indices, symbols of faces of the lower periods should always be taken, and face indices should be checked with the other zone crossing the face. For instance, to obtain the symbol of the face *K* (see Fig. 86), indices (211) and (110) can be added up.

The result is (321). Checking with the other zone between (100) and (221) we also obtain the symbol (321).

This construction can be used for a crystal of any system. In orientation of crystals of the trigonal and hexagonal systems for four axes it is necessary to take into account the peculiarities of symbols with four indices.

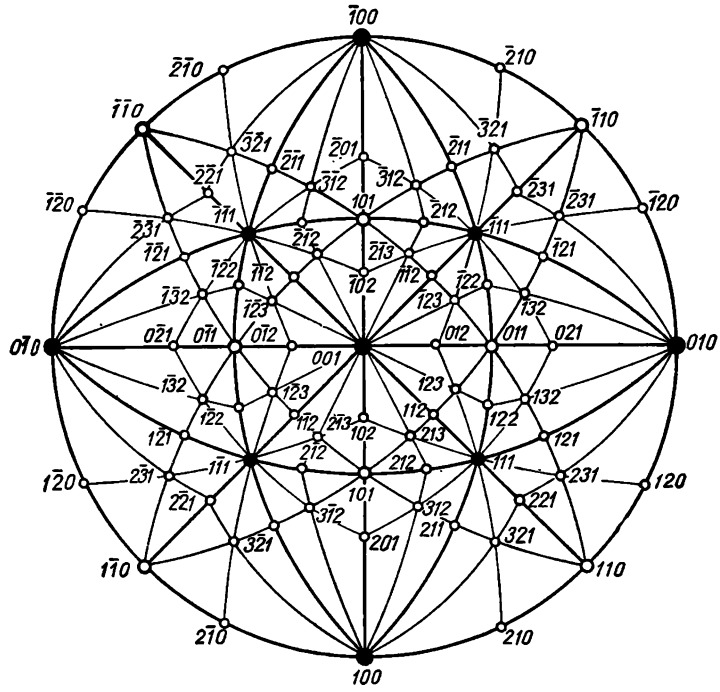


Fig. 87. Face symbols of the cubic complement

On closer inspection of the face complement (see Fig. 86), we notice the following peculiarity of the symbols: *the closer the face pole to the termination of an axis on the projection, the higher the index along this axis as compared with the other indices of its symbol.*

Fig. 87 shows the complement of faces for the cubic system, and Figs. 88 and 89—hexagonal complements in Bravais and Miller orientations respectively.

Crystallographic Calculations. The results of goniometric measurements enable us to determine the axial ratio $a : b : c$ (usually taken to be $a : 1 : c$), the interaxial angles α, β, γ, as well as the symbols of all the crystal faces. Crystallographic calculations consist in determining these values. They can be performed either with

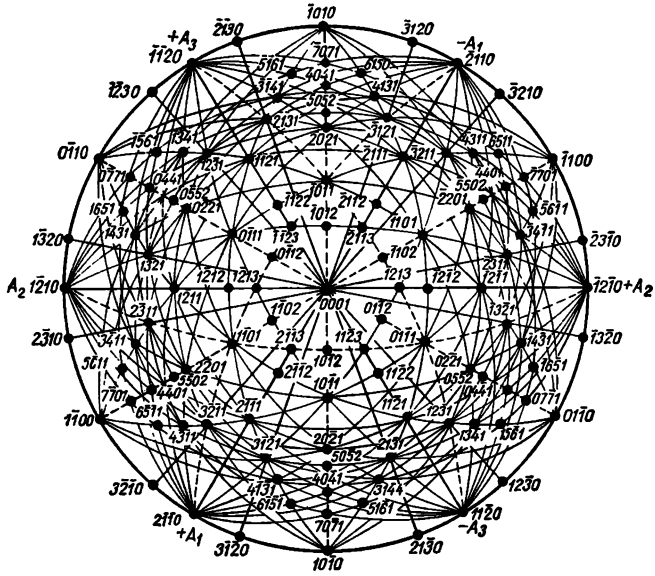


Fig. 88. Face symbols of the hexagonal complement for Bravais orientation

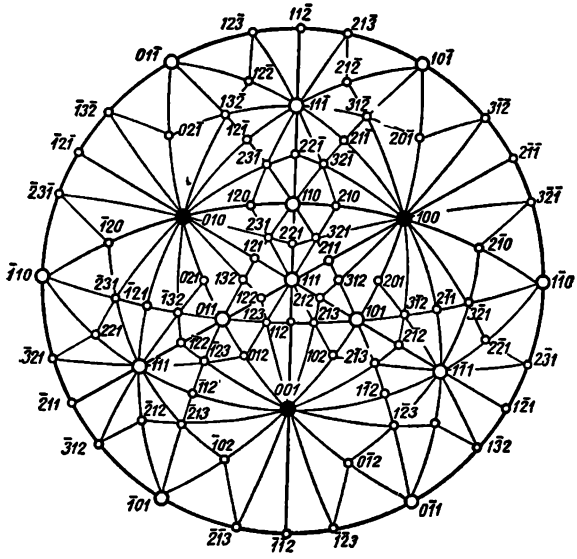


Fig. 89. Face symbols of the hexagonal complement for Miller orientation

the aid of a stereographic net, or mathematically with the aid of spherical trigonometry.

Let us imagine a face ABC (Fig. 90) giving intercepts OA, OB, and OC, and a normal to the face OP on the coordinate axes X, Y, Z.

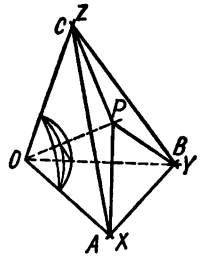


Fig. 90. A drawing for the cosine method

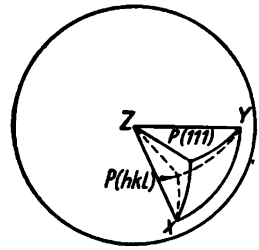


Fig. 91. A drawing for the cosine method on a projection

The relationship between the three intercepts can be determined from the three right triangles OPA, OPB, OPC:

$$OA = \frac{OP}{\cos AOP}; \quad OB = \frac{OP}{\cos BOP}; \quad OC = \frac{OP}{\cos COP}.$$

The angles AOP, BOP, and COP between the normal OP and the corresponding coordinate axes will be denoted for brevity by P_X, P_Y, P_Z. Thus, we shall have

$$OA:OB:OC = \frac{1}{\cos P_X}:\frac{1}{\cos P_Y}:\frac{1}{\cos P_Z}. \tag{7}$$

This relationship is true for any face intersecting all the three reference axes. For instance, for a unit face, a normal to which we shall denote by $P_{(111)}$ or simply (111), we shall have:

$$a:b:c = \frac{1}{\cos(111)_X}:\frac{1}{\cos(111)_Y}:\frac{1}{\cos(111)_Z}; \tag{8}$$

$$a:1:c = \frac{\cos(111)_Y}{\cos(111)_X}:1:\frac{\cos(111)_Y}{\cos(111)_Z}. \tag{8a}$$

The axial angles α, β, γ are determined from a diagram, insofar as $\alpha = COB$, $\beta = COA$, and $\gamma = BOA$. The symbol (hkl) in Millerian indices (page 75) for any face ABC is obtained by dividing a, b, c by the parameters of the face, i.e.:

$$h:k:l = \frac{a}{OA}:\frac{b}{OB}:\frac{c}{OC}.$$

Proceeding from the equation (2), we can write:

$$h:k:l = \frac{\cos P_X}{\cos(111)_X}:\frac{\cos P_Y}{\cos(111)_Y}:\frac{\cos P_Z}{\cos(111)_Z}. \tag{9}$$

Considering the stereographic projection (Fig. 91), we can see that all the values required for the calculation, can be determined graphically, simply by measuring the arcs of the great circles. Thus, having measured the arcs ZY, ZX, and XY we shall have the axial angles α, β, γ. In turn, we obtain the axial ratio by substituting the cosines of the angles subtended by the arcs $(111)_X$, $(111)_Y$, $(111)_Z$ into the equation (8). And finally the cosines of the angles subtended by the arcs $(hkl)_X$, $(hkl)_Y$, and $(hkl)_Z$ enable us to determine with the aid of the formula (9) the indices for any crystal face.

With quadrinomial indices of the hexagonal system calculations are first made to obtain three indices—two on the horizontal axes, and one on the vertical axis; the fourth index is then found using the equation:

$$h+k+i=0.$$

The accuracy of the graphical method is usually quite sufficient in determining face symbols. The axial ratio and the angles α, β, and γ must be calculated. This is done with the aid of the equation:

$$\cos\alpha_{(1,2)}=\cos\rho_1\cos\rho_2+\sin\rho_1\sin\rho_2\cos(\varphi_1-\varphi_2), \qquad (10)$$

where $\alpha_{(1,2)}$=angle between any two points (*1*) and (*2*) on a sphere or a pole on a projection

$\rho_1\varphi_1$ and $\rho_2\varphi_2$=spherical coordinates of the points.

The coordinates φ_p and ρ_p of the pole of the arc passing through two points (*1* and *2*) are calculated from the following equations:

$$\tan\varphi_p=-\frac{\tan\rho_1\cos\varphi_1-\tan\rho_2\cos\varphi_2}{\tan\rho_1\sin\varphi_1-\tan\rho_2\sin\varphi_2}; \qquad (11)$$

$$\cot\rho_p=-\tan\rho_1\cos(\varphi_p-\varphi_1); \qquad (12)$$

$$\cot\rho_p=-\tan\rho_2\cos(\varphi_p-\varphi_2). \qquad (12a)$$

The same equations can be used for more accurate calculations of indices. For each system one needs a definite minimum of measured angles which will serve as the basis for calculations. In the cubic system this minimum is 0, in the tetragonal and hexagonal systems—1, in the orthorhombic system—2, in the monoclinic system—3, and in the triclinic system—5 (inversely proportional to the degree of symmetry of the system). For accurate calculation of the coordinates of a given face the face is taken as the pole of the arc of a great circle, and the equations (12) and (12a) are applied. The circle is so selected that it contains two points of known coordinates. If there is no such circle, it should be constructed in the same way, i.e., two possible points of the circle are taken as poles, and a corresponding circle with two known points is found for each of the poles. The procedure is repeated until the number of angles constructed or measured on a crystal is sufficient for the respective system.

The method of making crystallographic calculations described above is by no means the only one.

CHAPTER VIII

Crystallochemical Analysis and the Law of Crystallographic Limits

We have learned the three principal laws of crystallography: the law of constancy of angle, the law of symmetry, and the law of rational indices (whole numbers). We have learned that there are 32 symmetries of forms of growth and accordingly 32 crystal classes. On the basis of the similarity of crystallographic constants the classes combine giving larger divisions or systems, of which there are seven: triclinic, monoclinic, orthorhombic, trigonal, tetragonal, hexagonal, and cubic. Is there any connection between these systems? Unsuccessful attempts at finding a connection, thus laying the foundation for a rational systematic classification of crystals, were made by several crystallographers.

The problem was solved by Fedorov. He discovered the law of crystallographic limits, in accordance with which the *ideal* crystals are those of the tetragonal and hexagonal systems. Crystals of all the other systems are derivatives of the ideal ones and can be derived from them by homogeneous deformations: extension and compaction. Fedorov gave the following definitions of the two deformations.

1. By extension of a three-dimensional figure is meant such deformation of the figure as a result of which only one plane, called the extension plane, retains its initial position, while all the other planes parallel to it are translated in a direction called the direction of extension, and the distances of these planes from the extension plane are then proportional to their original distances from the extension plane. The measure of extension is the projection of the distance of translation of a plane, located at a unit distance from the extension plane, on the perpendicular to the plane. If the distance of translation is unity, the figure will naturally suffer no alteration; if the distance is greater than unity, we shall have positive extension. If the distance is less than unity, we shall have compression which can be termed negative extension.

2. Compaction of a three-dimensional figure is such an alteration in which only one plane, called the compaction plane, remains statio-

nary, while all the other planes parallel to it are translated within themselves in a certain direction, called the compaction direction, by distances proportional to their distances from the compaction plane.

The measure of compaction is the translation of a plane which is parallel to the compaction plane and is located at a unit distance from

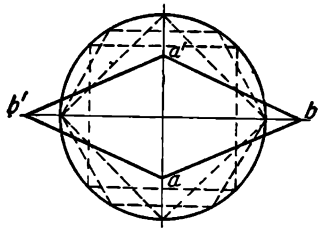


Fig. 92. Positive and negative extension

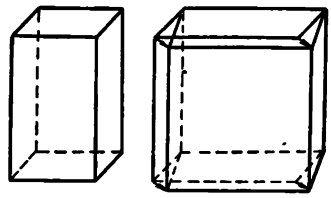


Fig. 93. Translation from rhombic to monoclinic figure by compaction

it. It can be seen from the above definition that the direction of compaction is parallel to the compaction plane.

A tetragonal prism, for instance, can be converted into a rhombic one by positive extension along *bb'* (Fig. 92) or by negative extension (compression) along *aa'*. A rhombic figure can be converted into a monoclinic one by way of compaction (Fig. 93).

What effect will these deformations have on the external habit and structure of a crystal? To answer this question let us first analyse the following constructions (Fig. 94). Let us imagine a crystal in the form of a cube with faces—plane nets—composed of squares. All the three pairs of its parallel faces are of uniform density. (The density of a face is the number of nodes per unit surface.) Let us subject the cube to positive extension along the vertical fourfold axis. The cube, supposedly elastic, will appear as shown in Fig. 95. Now the faces of the new figure will not be of uniform density. The upper and the lower faces will have retained their former density, but the density of the vertical faces will have decreased proportionately to the extension. If we subject the cube to negative extension—compression—along the same axis, we shall obtain the figure shown in Fig. 96. How will the densities of faces have altered in this case? The densities of the upper and the lower faces will have remained unchanged, while the densities of the vertical faces will have increased.

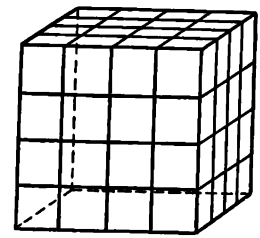


Fig. 94. Plane nets of cube faces

What effect do such deformations have on the habit and properties of real crystals? In the first case with positive extension along a vertical axis, the upper and the lower faces become denser, i.e., mechanically stronger, while the vertical faces change in the opposite direction. Hence, we shall expect the upper and the lower faces to be well developed and to have smooth plane surfaces, the vertical faces to be poorly developed, the crystal to be laminar in habit and to split readily along planes perpendicular to the vertical axis. In the second case, with negative extension along the vertical axis, we shall expect the crystal to have well developed vertical faces, poorly developed top and bottom faces, and a habit elongated along the vertical axis.

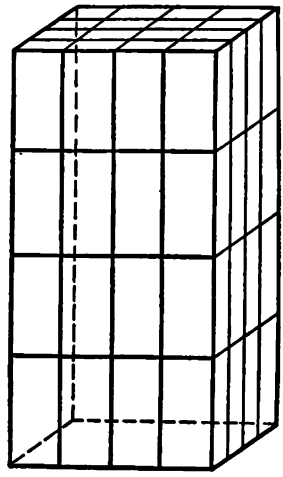


Fig. 95. Plane nets of cube faces after positive extension along L^4 axis

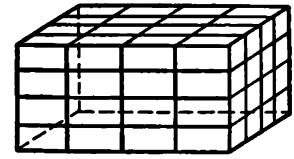


Fig. 96. Plane nets of cube faces after negative extension along L^4 axis

The law of crystallographic limits enabled Fedorov to arrange all crystallographically analysed compounds in a strictly defined order and to develop a new method of analysing compounds by the form of their crystals. This is known as crystallochemical analysis, and is one of the greatest achievements of Russian science.

Fedorov did a tremendous amount of work in compiling analytical tables which were published under the title *Das Kristallreich* (Petrograd, 1920) and which included all the crystals that had ever been measured.

These tables are used in the same way as those in biology, i.e., the name of an animal or a plant is found in the tables from the description of its characteristic features. A constant and characteristic morphological feature of crystals is the value of interfacial angles. It would seem sufficient to measure these angles with a goniometer in order to determine the name of the crystal from the tables. Actually it is not so simple, and for the following reasons.

1. Crystals of the same substance may comprise combinations of various simple forms. Consequently, their interfacial angles may be different.

2. Orientation of a crystal (i.e., selection of definite directions for coordinate axes and of a definite face for a unit face) is not governed by any strict rules. This is especially true of crystals of low symmetries. A matchbox, for instance, which has a $3L^2 3PC$ symmetry of the orthorhombic system, can be oriented in six different ways (Fig. 97), each of which will be correct. A change in orientation involves changes in the constants of the crystal and in the symbols of its faces. Therefore, compilation of analytical tables for crystals is a highly complicated task. Fedorov evolved methods of correctly and uniquely orienting crystals for this purpose. These methods are based on two general laws of crystallography: (1) the law of maximum density of faces of crystals with simple forms (see Ch. IX); and (2) the law of crystallographic limits. In accordance with the latter, crystals of the tetragonal and hexagonal systems are considered to be ideal. Crystals of all the other systems can be derived from the ideal ones by homogeneous deformation, i.e., extension (positive or negative) and compaction. The principle of minimum deformation should be observed in transition from an ideal crystal to one of another system. The rhombic prism shown in cross-section in Fig. 92 can be transformed into the ideal—tetragonal or hexagonal—by a single positive extension along *aa'* or a negative extension along *bb'*.

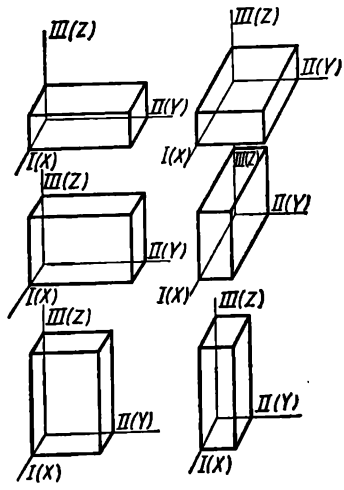


Fig. 97. Six orientations of a matchbox

Compaction is also necessary for transition to monoclinic and triclinic crystals. Fig. 93 shows the transition from a rhombic crystal to a monoclinic one. In accordance with the law of sequence of development of simple forms, faces with the densest nets are the first to develop on the crystal. If this law were followed ideally, we should have on our crystal a combination of the forms $a, b, c \ldots n$ with face densities $p_1, p_2, p_3 \ldots p_n$ decreasing from p_1 to p_n. Real crystals usually show some deviation from the ideal sequence of forms. For instance, the form with the face density p_2 may be completely undeveloped. If the sum of net densities, in case of the ideal sequence, is designated by $p_1+p_2+p_3+\ldots+p_n=I$, and the same sum for a real

crystal is designated by R, then the ratio $\frac{R}{I}$ will be a regular fraction close to unity. $V = \frac{R}{I}$ was named by Fedorov the *value of orientation*. For the ideal sequence $V=1$, but usually it is 0.9 or 0.8. The value of orientation V is the criterion of correct orientation. The closer V is to unity, the truer is the orientation. But the sequence of simple forms as regards net densities depends on crystal structure. Prior to finding the concrete values of I and R it is necessary to determine the type of structure of the crystal in accordance with Fedorov's theory of parallelohedra.

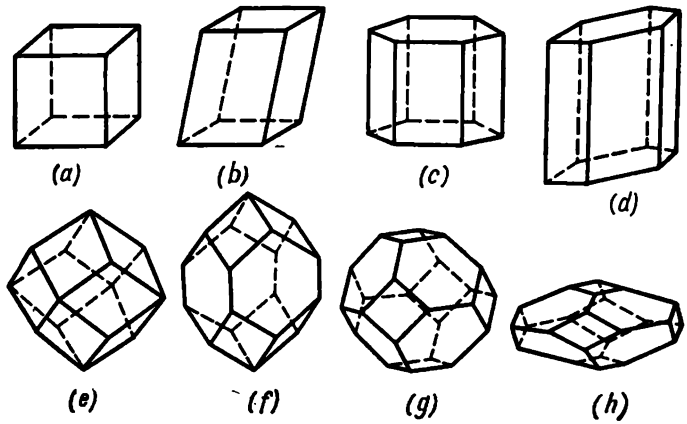


Fig. 98. Fedorov parallelohedra:
(a) and (b) triparallelohedra; (c) and (d) tetraparallelohedra; (e) and (f) hexaparallelohedra; (g) and (h) heptaparallelohedra

Fedorov applied the term of "parallelohedra" to geometrical figures which would completely fill up a space if arranged in parallel positions. Each parallelohedron is bounded by pairs of equal and parallel faces which can be only tetragonal or hexagonal. Fedorov proved that there could be only four types of parallelohedra differing from each other in the number of pairs of faces (Fig. 98):

(1) triparallelohedron bounded by three pairs of parallel faces, the most symmetrical or typical figure being a cube;

(2) tetraparallelohedron bounded by four pairs of parallel faces, a typical representative is a polyhedron consisting of a combination of a hexagonal prism and a pinacoid (see page 113);

(3) hexaparallelohedron with six pairs of parallel faces, a rhombic dodecahedron being the most symmetrical figure;

(4) heptaparallelohedron with seven pairs of parallel faces, being a combination of a cube and an octahedron.

Four types of structure correspond to these parallelohedra: hexahedral, prismatic, dodecahedral, and octahedral. The first of these corresponds to the primitive cubic lattice, the second to the hexagonal base-central lattice, the third and the fourth to the face-centred and body-centred cubic lattices respectively.

By homogeneous deformation (extension and compaction) the typical parallelohedra can be converted into other, less symmetrical, figures. Fedorov distinguished two types of crystals: cubic and hexagonal. The first type has three structures: hexahedral (*h*), octahedral (*o*), and dodecahedral (*d*). The second type has only one prismatic structure. Determining the proper orientation for monoclinic and triclinic crystals involves the finding of yet another value, *W*, which was named by Fedorov the *probability of orientation*; this value includes the cosine of the angle of deviation of the axis of the principal prismatic zone from 90° for tetragonaloidal crystals and from 60° for hexagonaloidal and trigonaloidal crystals.

In order to find a substance in Fedorov's analytical tables, it is necessary to do the following:

(1) to measure several (10-15) crystals with a goniometer;

(2) to make a projection of the results of measurements;

(3) to examine 30 to 50 crystals in order to determine the sequence of development of simple forms;

(4) to orient the crystals properly on the basis of the projection and the examination data;

(5) after finding the substance in the tables, to conduct, as a double check, some tests of physical properties mentioned in the tables.

Crystallochemical analysis is one of the major achievements of crystallography. Its advantages are self-evident, while there are two disadvantages worth mentioning: (1) much work is required to determine proper orientation; (2) it is impossible to analyse crystals of the cubic system, as the interfacial angles are the same for all substances.

Fedorov's students, A. K. Boldyrev and T. V. Barker, suggested the use of new, simpler methods, as the original method of crystallochemical analysis had not found universal recognition because of the difficulties involved in its use. Determining the nature of the compound with the aid of Fedorov's tables is done in the following sequence: (1) angles of crystals are measured; (2) Fedorov's unique orientation is determined; (3) the type of structure is determined; (4) finally, on the basis of the previous operations, the compound itself is found. The most difficult is the second stage, which can be carried out only by an experienced crystallographer. Barker suggested eliminating the third stage and replacing the second by his own unique orienta-

tion, which is much simpler than Fedorov's. The basic principle of Barker's orientation is that a correct orientation will result if the simplest forms entering into the combination are designated by symbols with the simplest indices.

Boldyrev suggested eliminating the second and the third stages. His method consists only of the measurement of crystal angles and the determination of the substance. He managed to dispense with unique orientation by giving a very large number of interfacial angles in his determinative tables. In these tables all the substances are divided into minerals and non-minerals. Beside interfacial angles, all the data available in literature are given for every substance. These data include: drawings of the more common habits, crystal class, space group, spacings between rows along crystallographic axes, data on twinning, character of the face sculpture, cleavage, specific gravity, hardness, colour, optical constants, melting point, solubility.

As a result, the determinative tables can now be used by a great many specialists in different branches of science.

CHAPTER IX

Forms of Crystal Growth

Real and Ideal Forms. The form of each individual crystal depends on the conditions of its growth. Therefore, corresponding faces of several crystals may have entirely different development. The symmetry of a crystal is thus concealed and can be detected only from the correct arrangement of interfacial angles.

The true symmetry of crystal growth of a substance can be shown in the following manner:

(1) its ideal form should be determined, i.e., the form which it would have if all its faces were uniformly developed;

(2) it should be ascertained by additional examination whether the symmetry found with the aid of the ideal form agrees with the symmetry of the physical properties of the substance.

The ideal form can be constructed on spherical projection (page 43). By drawing planes tangent to the sphere through all the polar points and taking into account the rates of growth of individual faces we shall obtain a polyhedron which will represent our ideal form; it is one of the possible forms of a crystal of the given substance.

In order to understand the morphology of crystals it is first necessary to become acquainted with geometrical figures which may occur in crystals and which make up the ideal form.

Simple Forms and Combinations. Let us imagine a spatial arrangement of a given complement of elements of symmetry corresponding to one of the 32 crystal classes, e.g., L^4PC and an arbitrary plane K_1 (Fig. 99). Let us assume the plane to be parallel to the fourfold axis. Now we shall carry out the operations relevant to these elements. The L^4 axis brings the plane K_1, by three successive rotations through 90°, into positions K_2, K_3, K_4. The plane P and the centre of symmetry cause no changes in the planes thus obtained and develop no new ones. The planes K_1, K_2, K_3, and K_4 intersect and form a square prism which is open at the top and at the bottom; this is a simple form.

Let us take the initial plane K_1 perpendicular to the L^4 axis (Fig. 100). Rotation about the axis leaves it in its former position,

but the plane of symmetry P and the centre of symmetry C cause the appearance of a new plane K_2. The two planes, K_1 and K_2, form a figure consisting of two parallel planes; it is also a simple form.

Let us take a third case: the initial plane is inclined to the L^4 axis and to the plane of symmetry P (Fig. 101). Rotation through 90° about the axis produces three new planes: K_2, K_3, K_4; all the four planes intersect and converge at one point producing a pyramid with a square base. The plane of symmetry P causes the appearance of a similar but inverted pyramid below (planes K_5, K_6, K_7, K_8). All the eight planes constitute a double pyramid, or a bipyramid, with a square section. This is the third simple form.

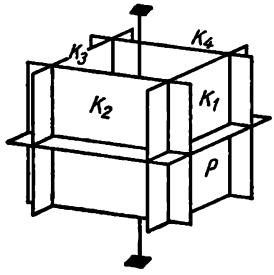


Fig. 99. Derivation of simple forms of the symmetry L^4PC; face is parallel to L^4

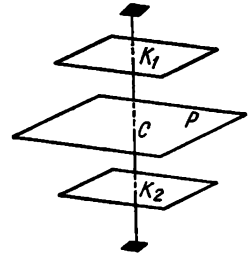


Fig. 100. Derivation of simple forms for the symmetry L^4PC; face is perpendicular to L^4

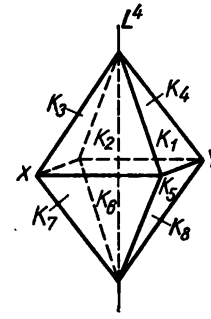


Fig. 101. Derivation of simple forms for the symmetry L^4PC; face is inclined to L^4

Now the following definition will be clear: *a simple form is a figure which can be derived from one given plane by the action of all the elements of symmetry of a class.*

Before we draw any conclusions, let us discuss another example.

Let us take a combination of elements of symmetry corresponding to the symmetry formula L^2PC (the rhombic-prismatic class of the monoclinic system). The initial plane (face) (Fig. 102) is again taken in three different positions. It is evident that here also three cases are possible:

(1) the face is parallel to the plane of symmetry and perpendicular to the L^2 axis;

(2) the face is parallel to the L^2 axis and perpendicular to the plane of symmetry;

(3) the face is inclined to the axis and to the plane of symmetry.

In Fig. 102 the L^2 axis lies in the plane of the diagram, the plane P and the face AA_1 are perpendicular to it. In the first case (Fig. 102, *a*) the plane P causes the appearance of a new face, BB_1. Rotating the

pair of parallel faces about the L^2 axis we obtain no new faces, since the AA_1 and BB_1 faces rotate within themselves. The action of the centre of symmetry does not add any new faces either*. Consequently, the action of all the elements of symmetry of the L^2PC class on the face AA_1 produces only two parallel faces—AA_1 and BB_1. This is what is called a simple form. In the second case (Fig. 102, *b*) the face AA_1 is perpendicular to the plane of symmetry. Therefore, this

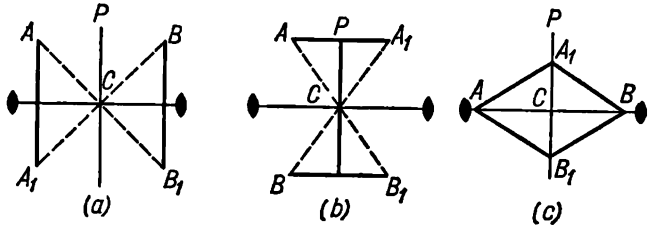


Fig. 102. Derivation of simple forms for the symmetry L^2PC

plane does not cause the appearance of new faces, but rotation of the face AA_1 through 180° about the L^2 axis produces a new face, BB_1. In the third case (Fig. 102, *c*) the face AA_1 is inclined to the plane and to the axis of symmetry; the plane P causes the appearance of a new face, A_1B. Now we have a pair of intersecting faces. Rotation of this pair about the L^2 axis through 180° produces two new faces, BB_1 and B_1A. Now we have four faces in all.

By successively taking the complements of elements of symmetry of all the 32 classes and by constructions analogous with the ones above, we can derive all the possible simple forms in polyhedral crystals. Here are some guiding principles.

1. The characteristic feature of a simple form is the crystallographic equivalence of all of its faces.

2. The rates of growth of all the faces of a simple form are similar under similar conditions.

3. Crystals are rarely bounded by one simple form. More often there are so-called *combinations* of several simple forms.

4. Simple forms may be open, as those shown in Figs. 99 and 100, or closed, i.e., space-enclosing (Fig. 101).

5. The more elements of symmetry there are in the complement of a class, the more complicated and diverse are its simple forms.

6. When the initial plane is taken in a general position, the simple form derived is called a *general form*, or a form of a general type.

7. When the initial plane is taken in a special position, the resulting form is called a *special form*.

* This is a convincing proof of C being the resultant element for the L^2 axis and the plane P.

8. The position of the initial plane is general when it is not perpendicular or parallel to any of the symmetry elements of the complement and does not cut similar elements at the same angles. This is true for general forms of the lower and intermediate systems. Only the second part of the definition is true for general simple forms of the cubic system. Hence, the general simple form of the cubic system is a form whose faces do not cut similar elements of symmetry at the same angles.

9. Two mirror-equivalent simple forms or combinations are called *enantiomorphous*, unless they are congruent to one another.

10. Open forms (not space-enclosing) can be present only in combinations.

Symbols of Simple Forms. Insofar as all the faces of a simple form have been derived from one initial plane, they must have similar symbols. Individual indices may be positive or negative, their order may vary, but their numerical values must be the same for all the faces of the form.

In one of the examples discussed, with L^4 taken as the reference axis Z, and two mutually perpendicular directions in the plane of symmetry—as the X and Y axes—the faces had the following symbols.

1. The first example, the 1st position (see Fig. 99): faces K_1—(010); K_2—(100); K_3—(0$\bar{1}$0); K_4—($\bar{1}$00).

2. The first example, the 2nd position (see Fig. 100): faces K_1—(001); K_2—(00$\bar{1}$).

3. The first example, the 3rd position (see Fig. 101): faces K_1—(111); K_2—(1$\bar{1}$1); K_3—($\bar{1}\bar{1}$1); K_4—($\bar{1}$11); K_5—(11$\bar{1}$); K_6—(1$\bar{1}\bar{1}$); K_7—($\bar{1}\bar{1}\bar{1}$); K_8—($\bar{1}$1$\bar{1}$).

If it is to be shown that the symbol refers not only to an individual face, but to the entire simple form, it is then enclosed in braces, for instance: {100}, {001}, {101}.

Unfortunately this rule is not very strictly observed at present, and the symbols of simple forms are parenthesized as the symbols of individual faces, sometimes resulting in confusion.

Derivation of Simple Forms from Stereographic Projections. The method of derivation of simple forms which has been demonstrated becomes highly inconvenient when the crystal class has a large number of elements of symmetry. Therefore, it is much more sensible to derive simple forms with the aid of stereographic projections.

Let us take the $L^2 2P$ class of the orthorhombic system as an example (Fig. 103). The initial plane is taken in all the positions possible for this class.

1. The initial plane is inclined towards one plane of symmetry (P_1) and perpendicular to another (P_2); hence, the pole of its normal is on the plane P_2—position *1* in Fig. 103. The twofold axis and the plane P_1 cause the appearance of another face—position *1'*. P_2 has

no effect on the given face, as it is perpendicular to it. We therefore obtain a simple form consisting of two intersecting faces (in the shape of a roof). If we take a point on the plane P_1, we shall arrive at the same result.

2. Let us take a face in the same plane P_2, but at *2*, the point of its intersection of the primitive circle. In the position *2'* we obtain a parallel face. A simple form results with two parallel faces.

3. Let us take a plane perpendicular to all the elements of symmetry. A normal to it is at *3*, the point of intersection of the two planes of symmetry, i.e., at the terminal point of the twofold axis. None of the three symmetry elements have any effect on the face, i.e., none of them produce any new planes. There remains the single initial face which is in this case a simple form.

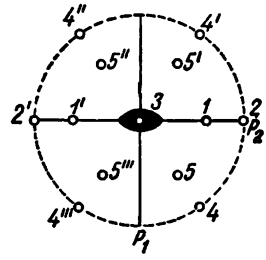


Fig. 103. Derivation of simple forms for the symmetry $L^2 2P$ on a projection

4. The face *4* is in such a position that a normal to it is in the primitive circle. The plane P_2 develops from it the face *4'*, and the plane P_1 develops from the two faces, *4'''* and *4''*, respectively. The twofold axis transfers the face *4* to the already existing point *4''*, and the face *4'*, to the point *4'''*, i.e., it produces nothing new (an instance of the resultant element of symmetry). We obtain four faces parallel to one direction, i.e., a prism of rhombic section.

5. The final version: the face *5* taken inside one of the quadrants is a face in a general position; we are to derive a general simple form. The plane P_2 produces the face *5'*, the plane P_1 produces the faces *5'''* and *5''*; the axis adds nothing. We obtain a form with four faces intersecting at one point, i.e., a pyramid with a rhombic base.

We cannot take a point (a pole) on the bisectrix of the angle P_1P_2, as this would contradict the condition $a \neq b$ evolved for crystals of the orthorhombic system.

Having made a similar analysis of each of the 32 crystal classes, we obtain all the simple forms which can occur in crystals, totalling 47. As has been shown, each derived form has a definite crystallographic name: cube, octahedron, trigonal prism, etc. Thus, there are altogether 47 simple forms with different names.

Crystallographically Differing Forms. One and the same form can occur in several crystal classes, e.g., the cube occurs in all the five classes of the cubic system.

Forms differing in name or symmetry or both are considered different crystallographically, consequently, there are five crystallographically different cubes. The difference can be shown by different shading of the cube faces (Fig. 104). In real crystals the diffe-

rence has been established by a study of the physical properties of face surfaces, primarily of etch figures and natural striation. Fig. 105 shows a crystal of pyrite, FeS_2, with natural striation of the faces of a cube, which definitely indicates the $3L^24L_6^33PC$ crystal class.

Fig. 104. Cube faces with five symmetry classes of the cubic system

Fig. 106 shows etch figures on prisms of apatite, $Ca_5(Cl, F)P_3O_{12}$, and calcite, $CaCO_3$. The arrangement and the shape of the etch figures clearly show that apatite has a sixfold axis and a perpendicular

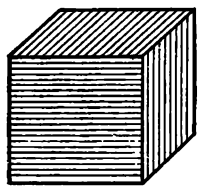


Fig. 105. Natural striation on pyrite cube faces

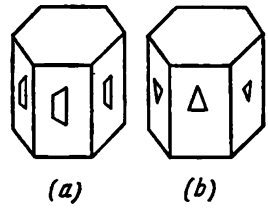


Fig. 106. Etch figures on apatite (*a*) and calcite (*b*) faces

plane of symmetry, i.e., belongs to the L^6PC crystal class, and that calcite has an L_6^3 axis, three vertical planes of symmetry, three twofold axes, and a centre of symmetry, i.e., belongs to the $L_6^33L^23PC$ crystal class.

SIMPLE FORMS OF THE LOWER SYSTEMS

1. A form consisting of a single face is called a *pedion* (Fig. 107, *a*). It is so situated on a crystal that it is not repeated by any of the elements of symmetry.

2. In two-faceted forms the faces may (1) intersect or (2) be parallel to one another. In the first case we have a *dihedron*, or *dome* or a *sphenoid* (Fig. 107, *c* and *d*), in the second case a *pinacoid* (Fig. 107, *b*).

3. Classes of the lower systems have no three-faceted forms. Three simple forms can be constructed from four faces:

(1) a rhombic prism (Fig. 107, *e*), in which all the four faces intersect along parallel edges; this prism has a rhombic cross-section;
(2) a rhombic tetrahedron (Fig. 107, *f*), in which the faces are so arranged that on intersection they enclose a space and have the appearance of irregular triangles; the figure is rhombic in cross-section;
(3) a rhombic pyramid (Fig. 107, *g*), in which the faces intersect along edges converging at one point; any section normal to the altitude of the figure is rhombic.

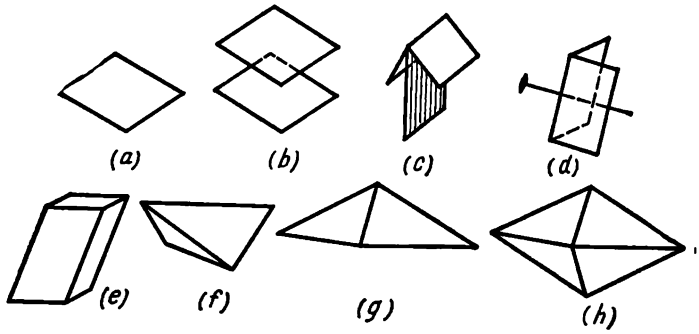


Fig. 107. Simple forms of lower systems

4. The last of the simple forms of the lower systems consists of eight faces. This is a rhombic bipyramid (Fig. 107, *h*). It consists, as it were, of two rhombic pyramids joined at their bases.

The majority (five out of seven) of the simple forms of the lower systems are open. They consist of a small number of faces, because the classes of these systems have few elements of symmetry and no axes of a higher degree.

SIMPLE FORMS OF THE INTERMEDIATE SYSTEMS

Here we have a much greater variety in external appearance and in the number of faces of simple forms. It will be more convenient to describe the forms in a somewhat different order.

1. As in the lower systems, prisms are open forms made up by faces intersecting along parallel edges. Depending on the section normal to the main axis, shown above the figure, prisms are regarded as: trigonal (Fig. 108, *a*); ditrigonal (Fig. 108, *b*); tetragonal (Fig. 108, *c*); ditetragonal (Fig. 108, *d*); hexagonal (Fig. 108, *e*); and dihexagonal (Fig. 108, *f*). It should be noted that ditrigon, ditetragon, and dihexagon are the names of figures obtained by doubling the number of sides of a regular triangle, quadrangle (tetragon), and hexagon.

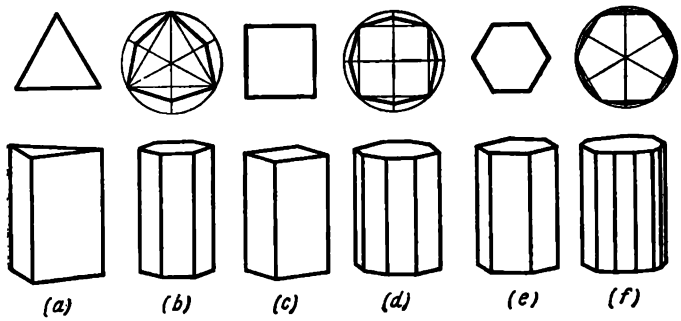


Fig. 108. Prisms of intermediate systems

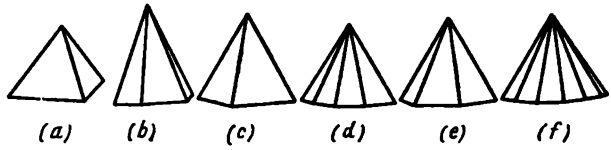


Fig. 109. Pyramids of intermediate systems

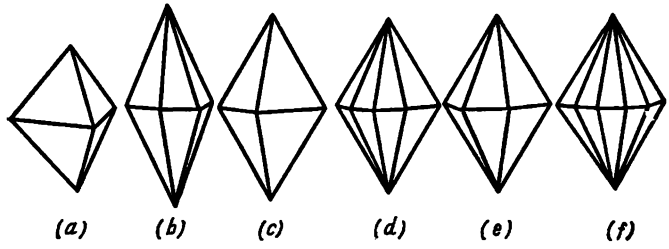


Fig. 110. Bipyramids of intermediate systems

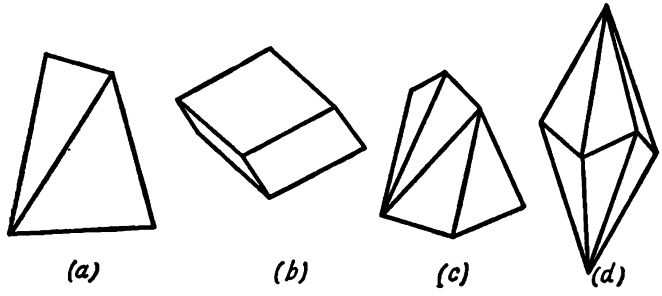


Fig. 111. Tetragonal tetrahedron, rhombohedron, scalenohedra

2. A similar nomenclature has been adopted for pyramids and bipyramids. We shall not repeat it. These forms are shown in Figs. 109 and 110.

3. The forms of the rhombohedron, tetragonal tetrahedron, scalenohedron, and trapezohedron are characteristic in their own way.

Polyhedra whose faces have the form of scalene triangles are called *scalenohedra*, and polyhedra with faces in the form of trapezia are called *trapezohedra*.

A rhombohedron (Fig. 111, *b*) consists of six rhombic faces, three of which are above and three below, the three upper faces being turned relative to the lower ones through 60° about the main axis.

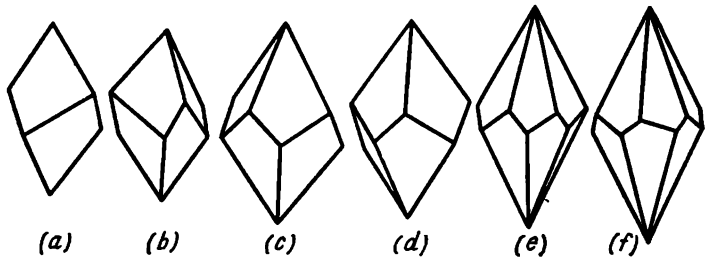


Fig. 112. Trapezohedra

A tetragonal tetrahedron (Fig. 111, *a*) resembles a rhombic one but is square in mid-section, and its faces have the form of isosceles triangles.

Tetragonal and ditrigonal scalenohedra are morphologically similar to the forms described above, but with twice the number of faces (Fig. 111, *c* and *d*). This doubling occurs in such a way that the faces of the tetrahedron and rhombohedron are halved along the symmetry plane normal to the corresponding face. These polyhedra should be called ditetragonal and dihexagonal, if the rule of naming the forms of intermediate systems according to the middle section is to be strictly observed, because they are ditetragonal and dihexagonal in cross-section.

Trapezohedra—trigonal, tetragonal and hexagonal (Fig. 112)—resemble bipyramids, but differ essentially from the latter in that they have no symmetry planes. The upper pyramid is turned relative to the lower one through a given angle which is not equal to half the elementary angle of rotation of the corresponding main axis. All trapezohedra are enantiomorphous and are therefore either of the right- or the left-hand variety (see page 54).

The pedion and the pinacoid are forms of the lower systems occurring in the intermediate systems.

SIMPLE FORMS OF THE CUBIC SYSTEM

The four threefold axes in all the crystal classes of the cubic system provide conditions for the formation of simple forms which radically differ from the forms of other systems.

All the simple forms of the cubic system are closed ones.

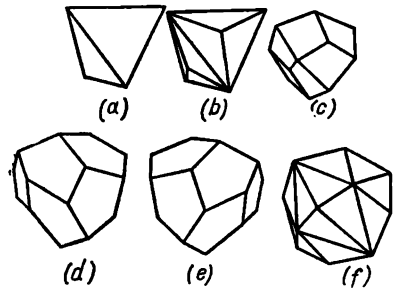


Fig. 113. Simple forms of the cubic system—a tetrahedron and its higher modifications

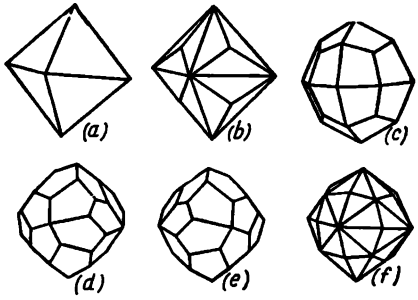


Fig. 114. Simple forms of the cubic system—an octahedron and its higher modifications

Very few forms have a small number of faces, and very rarely can this number be used as a diagnostic feature.

To facilitate the memorizing of the names of forms, they are best divided into three groups of five names each. The first and the second groups are similar: one of them contains forms that are complicated tetrahedra, the other—complicated octahedra (Figs. 113 and 114).

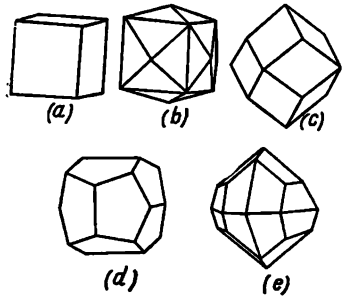


Fig. 115. Simple forms of the cubic system—a cube, a tetrahedron, a didodecahedron, a pentagonal dodecahedron, and a rhombic dodecahedron

Group I

1. Tetrahedron
2. Trigonal tritetrahedron
3. Tetragonal tritetrahedron
4. Pentagonal tritetrahedron
5. Hexatetrahedron

Group II

1. Octahedron
2. Trigonal trioctahedron
3. Tetragonal trioctahedron
4. Pentagonal trioctahedron
5. Hexoctahedron

The third group (Fig. 115) includes forms not listed in the first two groups.

Group III

1. Cube (hexahedron)
2. Tetrahexahedron
3. Pentagonal dodecahedron
4. Didodecahedron
5. Rhombic dodecahedron

In all cases the name consists of Greek numerals with the addition of the suffix "hedron". For instance, "octahedron" means eight-faceted ("octa"—eight, and "hedron"—face). The addition of the prefixes di-, tri-, etc., means double, triple (the number of faces) and so on. For instance, "trioctahedron" means an octahedron with three times eight faces. The preceding adjective indicates the shape of individual faces. For instance, "pentagonal trioctahedron" means that on an octahedron with three times the number of faces the latter have the shape of pentagons.

It is much easier to show the habit of simple forms diagrammatically than to describe them in words. Therefore, we shall give no special description of these forms. It should be noted that there are two enantiomorphous forms among them: the pentagonal tritetrahedron and pentagonal trioctahedron, which occur in the right- and left-hand varieties.

COMBINATIONS OF SIMPLE FORMS

As distinct from simple forms, combinations cannot be derived from a single initial plane and, consequently, have crystallographically dissimilar faces. The number of simple forms which together

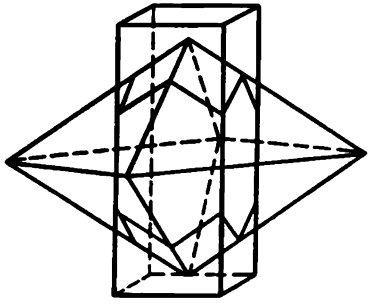


Fig. 116. Development of combinations: a prism and a bipyramid

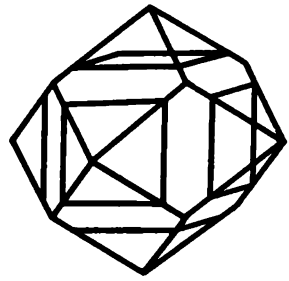


Fig. 117. Development of combinations: a cube and a rhombic dodecahedron

can produce a combination can be determined by the number of different faces of a figure.

The formation of combinations is shown in Figs. 116 and 117. In the first case we have a combination of a prism and a bipyramid, in the second—of a rhombic dodecahedron and a cube.

We shall not discuss in detail the technique of analysing combinations. We shall only mention the order in which the analysis should be carried out:

(1) the symmetry elements of a figure are determined, and hence the crystal class is found;

(2) the number of simple forms in the combination is determined, as well as the number of faces of each form;

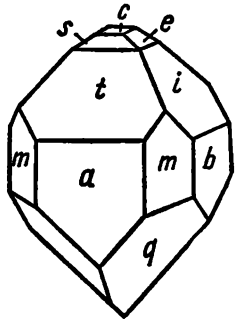


Fig. 118. Combination of forms in a calamine crystal

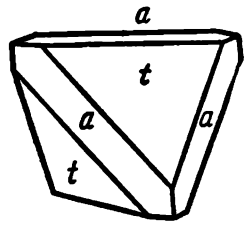


Fig. 119. Combination of forms in a sphalerite crystal

(3) the figure is compared with the simple forms of the given crystal class and the names of individual simple forms in the combination are established, taking into account the number of faces and their position relative to the symmetry elements.

The shape of faces should not be used as a basis, since in combinations the faces may have an entirely different appearance from the initial simple form. Thus, the faces of a cube may not be squares, those of a tetrahedron—not equilateral triangles, those of a rhombohedron—not rhombs, etc.

Let us analyse, for instance, the two combinations shown in Figs. 118 and 119.

1. In the combination shown in Fig. 118 (calamine, $Zn_2H_2SiO_5$), we have the following elements of symmetry: a twofold axis (vertically) and two symmetry planes intersecting along it at 90°. Thus, the crystal belongs to the rhombic pyramidal class of the orthorhombic system.

This class has five simple forms (see page 130): the pedion, pinacoid, dome, rhombic prism, and rhombic pyramid. Which of these forms participate in the formation of the combination? Let us count the number of different faces: *c*, *s*, *t*, *a*, *e*, *i*, *b*, *m*, *q*—nine in all. We have nine simple forms in the combination. The face *c* is not repeated

by any of the symmetry elements; it is therefore a pedion. Of the faces *s*, *t*, *e*, *i* there are two each, and each pair intersects if produced. Therefore, these faces make up four domes. Of the faces *a* and *b* there are also two of each of them, but they remain parallel if produced. These faces make up two pinacoids. There are four faces *q*, and they all converge at one point, forming a rhombic pyramid. There are also four faces *m*, but they intersect along parallel edges. This is a rhombic prism.

2. The combination shown in Fig. 119 (sphalerite, zinc blende, ZnS) has four threefold polar axes, three twofold axes and six planes

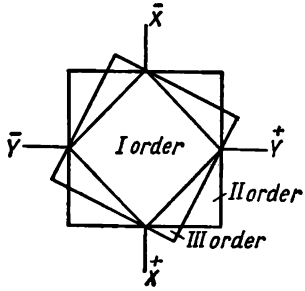


Fig. 120. Forms of different orders in the tetragonal system

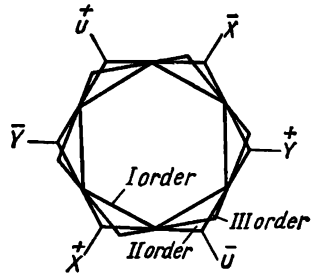


Fig. 121. Forms of different orders in the hexagonal system

of symmetry. The crystal belongs to the $3L_4^24L^36P$ class of the cubic system. It has two different faces. Thus, the combination has only two simple forms: *a* and *t*. From the number of faces we see that *a* is a cube (six faces), and *t*—a tetrahedron (four faces).

Sometimes the analysis is simpler than in these examples, while in other cases it is much more complicated. The latter is especially true of the cubic combinations in which we have several forms with an equal number of faces, the number thus losing its diagnostic importance.

In the Tables 6-10 simple forms for all systems are listed.

In some nomenclatures prisms, pyramids and bipyramids are divided into forms of the first, second and third order. Since this division often occurs in literature, it requires some explanation, although our modern nomenclature does not recognize it.

Forms of the first order are those which cut the *I* and *II* axes at equal angles. The tetragonal prism of the first order has the symbol {110}, the hexagonal prism—{11$\bar{2}$0}.

Forms of the second order are those whose faces are perpendicular to the axes *I* and *II* in the tetragonal system—symbol {100}. In the

Simple forms of the triclinic, monoclinic

Crystal class / Symbols	Triclinic system		Monoclinic	
	L^1	C	L^2	P
(*hkl*)	Pedion (1)*	Pinacoid (2)	Dihedron (2)	Dome (2)
(0*kl*)	Pedion (1)	Pinacoid (2)	Sphenoid (2)	Dome (2)
(*h*0*l*)	Pedion (1)	Pinacoid (2)	Pinacoid (2)	Pedion (1)
(*hk*0)	Pedion (1)	Pinacoid (2)	Sphenoid (2)	Dome (2)
(100)	Pedion (1)	Pinacoid (2)	Pinacoid (2)	Pedion (1)
(010)	Pedion (1)	Pinacoid (2)	Pedion (1)	Pinacoid (2)
(001)	Pedion (1)	Pinacoid (2)	Pinacoid (2)	Pedion (1)

Simple forms of

Crystal class / Symbols	L^4	$L^4 4L^2$	L^4PC
(*hkl*)	Tetragonal pyramid (4) *	Tetragonal trapezohedron (8)	Tetragonal bipyramid (8)
(*hhl*)	Tetragonal pyramid (4)	Tetragonal bipyramid (8)	Tetragonal bipyramid (8)
(*h*0*l*)	Tetragonal pyramid (4)	Tetragonal bipyramid (8)	Tetragonal bipyramid (8)
(*hk*0)	Tetragonal prism (4)	Ditetragonal prism (8)	Tetragonal prism (4)
(110)	Tetragonal prism (4)	Tetragonal prism (4)	Tetragonal prism (4)
(100)	Tetragonal prism (4)	Tetragonal prism (4)	Tetragonal prism (4)
(001)	Pedion (1)	Pinacoid (2)	Pinacoid (2)

* Figures in parentheses indicate the number of faces of the respective simple form.

Table 6

and orthorhombic systems

system	Orthorhombic system		
L^2PC	$3L^2$	L^22P	$3L^23PC$
Rhombic prism (4)	Rhombic tetrahedron (4)	Rhombic pyramid (4)	Rhombic bipyramid (4)
Rhombic prism (4)	Rhombic prism (4)	Dome (2)	Rhombic prism (4)
Pinacoid (2)	Rhombic prism (4)	Dome (2)	Rhombic prism (4)
Rhombic prism (4)	Rhombic prism (4)	Rhombic prism (4)	Rhombic prism (4)
Pinacoid (2)	Pinacoid (2)	Pinacoid (2)	Pinacoid (2)
Pinacoid (2)	Pinacoid (2)	Pinacoid (2)	Pinacoid (2)
Pinacoid (2)	Pinacoid (2)	Pedion (1)	Pinacoid (2)

Table 7

the tetragonal system

L^44P	L^44L^25PC	L^2_4	L^22L^22P
Ditetragonal pyramid (8)	Ditetragonal bipyramid (16)	Tetragonal tetrahedron (4)	Tetragonal scalenohedron (8)
Tetragonal pyramid (4)	Tetragonal bipyramid (8)	Tetragonal tetrahedron (4)	Tetragonal tetrahedron (4)
Tetragonal pyramid (4)	Tetragonal bipyramid (8)	Tetragonal tetrahedron (4)	Tetragonal bipyramid (8)
Ditetragonal prism (8)	Ditetragonal prism (8)	Tetragonal prism (4)	Ditetragonal prism (8)
Tetragonal prism (4)	Tetragonal prism (4)	Tetragonal prism (4)	Tetragonal prism (4)
Tetragonal prism (4)	Tetragonal prism (4)	Tetragonal prism (4)	Tetragonal prism (4)
Pedion (1)	Pinacoid (2)	Pinacoid (2)	Pinacoid (2)

Simple forms of

Crystal class / Symbols	L^3	$L^3 3L^2$
(*hikl*)	Trigonal pyramid (3) *	Trigonal trapezohedron (6)
($h0\bar{h}l$)	Trigonal pyramid (3)	Rhombohedron (6)
($hh\bar{2}hl$)	Trigonal pyramid (3)	Trigonal bipyramid (6)
(*hikl*)	Trigonal prism (3)	Ditrigonal prism (6)
($10\bar{1}0$)	Trigonal prism (3)	Hexagonal prism (6)
($11\bar{2}0$)	Trigonal prism (3)	Trigonal prism (3)
(0001)	Pedion (1)	Pinacoid (2)

Simple forms of

Crystal class / Symbols	L^6	$L^6 6L^2$	$L^6 PC$
(*hikl*)	Hexagonal pyramid (6) *	Hexagonal trapezohedron (12)	Hexagonal bipyramid (12)
($h0\bar{h}l$)	Hexagonal pyramid (6)	Hexagonal bipyramid (12)	Hexagonal bipyramid (12)
($hh\bar{2}hl$)	Hexagonal pyramid (6)	Hexagonal bipyramid (12)	Hexagonal bipyramid (12)
(*hikl*)	Hexagonal prism (6)	Dihexagonal prism (12)	Hexagonal prism (6)
($10\bar{1}0$)	Hexagonal prism (6)	Hexagonal prism (6)	Hexagonal prism (6)
($11\bar{2}0$)	Hexagonal prism (6)	Hexagonal prism (6)	Hexagonal prism (6)
(0001)	Pedion (1)	Pinacoid (2)	Pinacoid (2)

* Figures in parentheses indicate the number of faces of the respective simple

Table 8

the trigonal system

L^3P	L^3C	L^33L^23PC
Ditrigonal pyramid (6)	Rhombohedron (6)	Ditrigonal scalenohedron (12)
Trigonal pyramid (3)	Rhombohedron (6)	Rhombohedron (6)
Hexagonal pyramid (6)	Rhombohedron (6)	Hexagonal bipyramid (12)
Ditrigonal prism (6)	Hexagonal prism (6)	Dihexagonal prism (12)
Trigonal prism (3)	Hexagonal prism (6)	Hexagonal prism (6)
Hexagonal prism (6)	Hexagonal prism (6)	Hexagonal prism (6)
Pedion (1)	Pinacoid (2)	Pinacoid (2)

Table 9

the hexagonal system

L^6P	L^66L^27PC	L^3P	L^33L^24P
Dihexagonal pyramid (12)	Dihexagonal bipyramid (24)	Trigonal bipyramid (6)	Ditrigonal bipyramid (12)
Hexagonal pyramid (6)	Hexagonal bipyramid (12)	Trigonal bipyramid (6)	Hexagonal bipyramid (12)
Hexagonal pyramid (6)	Hexagonal bipyramid (12)	Trigonal bipyramid (6)	Trigonal bipyramid (6)
Dihexagonal prism (12)	Dihexagonal prism (12)	Trigonal prism (3)	Ditrigonal prism (6)
Hexagonal prism (6)	Hexagonal prism (6)	Trigonal prism (3)	Hexagonal prism (6)
Hexagonal prism (6)	Hexagonal prism (6)	Trigonal prism (3)	Trigonal prism (3)
Pedion (1)	Pinacoid (2)	Pinacoid (2)	Pinacoid (2)

form.

Table 10

Simple forms of the cubic system

Symbols \ Crystal class	$3L^34L^3$	$3L^34L^33PC$	$3L^34L^36P$	$3L^44L^36L^2$	$3L^44L^36L^29PC$
(*hkl*)	Pentagonal tritetrahedron (12) *	Didodecahedron (24)	Hexatetrahedron (24)	Pentagonal trioctahedron (24)	Hexoctahedron (48)
(*hhl*)	Tetragonal tritetrahedron (12)	Trigonal trioctahedron (24)	Tetragonal tritetrahedron (12)	Trigonal trioctahedron (24)	Trigonal trioctahedron (24)
(*hkk*)	Trigonal tritetrahedron (12)	Tetragonal trioctahedron (24)	Trigonal tritetrahedron (12)	Tetragonal trioctahedron (24)	Tetragonal trioctahedron (24)
(111)	Tetrahedron (4)	Octahedron (8)	Tetrahedron (4)	Octahedron (8)	Octahedron (8)
(*hk*0)	Pentagonal dodecahedron (12)	Pentagonal dodecahedron (12)	Tetrahexahedron (24)	Tetrahexahedron (24)	Tetrahexahedron (24)
(110)	Rhombic dodecahedron (12)	Rhombic dodecahedron (12)	Rhombic dodecahedron (12)	Rhombic dodecahedron (12)	Rhombic dodecahedron (12)
(100)	Hexahedron (cube) (6)	Hexahedron (cube) (6)	Hexahedron (cube) (6)	Hexahedron (cube) (6)	Hexahedron (cube) (6)

* Figures in parentheses indicate the number of faces of the respective simple form.

hexagonal system their faces cut the axes *I* and *III* at equal angles (the latter at the negative end), the symbol being $\{10\bar{1}0\}$.

Forms of the third order are those whose faces cut horizontal axes (*I* and *II* in the tetragonal system, *I*, *II*, *III* in the hexagonal system) at unequal angles (Figs. 120 and 121) and have symbols $\{210\}$, $\{21\bar{3}0\}$.

Pinacoids are also called first, second, of the first order, of the second order, depending on their position relative to the crystallographic axes. Some simple forms, e.g., the tetrahedron, pentagonal dodecahedron, rhombohedron, may be called positive or negative depending on their position.

Tetrahedra, trigonal tritetrahedra, tetragonal tritetrahedra, and hexatetrahedra are said to be *positive* if their symbols are $\{111\}$, $\{hkk\}$, $\{hhl\}$, and $\{hkl\}$ respectively, and *negative* if their symbols are $\{1\bar{1}1\}$, $\{h\bar{k}k\}$, $\{h\bar{h}l\}$, and $\{h\bar{k}l\}$ respectively.

Pentagonal dodecahedra and didodecahedra are considered to be in the *first position*, if they have symbols $\{hk0\}$ and $\{hkl\}$, and in the *second position*, if their symbols are $\{kh0\}$ and $\{hlk\}$. A rhombohedron is of the first order if it has the symbol $\{h0\bar{h}\bar{l}\}$, and of the second order if its symbol is $\{hh\bar{2}\bar{h}l\}$.

For the simple forms of the cubic system showh here $h>k>l$.

CHAPTER X

Distribution of Simple Forms by Classes

TRICLINIC SYSTEM

1. *Pedial class* (symmetry formula L^1). Crystals of this class have no elements of symmetry, but for axes of the first degree, which is equivalent to a complete absence of symmetry.

The only possible simple form is a pedion (see Fig. 107). Its symbol is $\{hkl\}$, where h, k, and l can be any positive or negative whole numbers, including ± 1 and 0. This class is represented by relatively few crystals.

Examples

(1) Calcium thiosulphate, $CaS_2O_3 \cdot 6H_2O$ (Fig. 122). $a : b : c = 0.7847 : 1 : 1.5179$; $\alpha = 72°24'$; $\beta = 98°32'$; $\gamma = 92°40'$; $a\{100\}$, $b\{010\}$, $c\{001\}$, $p\{110\}$, $m\{1\bar{1}0\}$, $o\{111\}$, $r\{101\}$, $q\{011\}$.

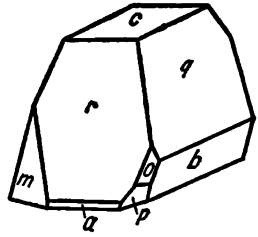


Fig. 122. Calcium thiosulphate

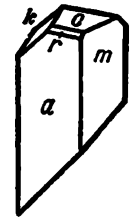


Fig. 123. Rubidium ferrocyanide

(2) Rubidium ferrocyanide, $Rb_4Fe(CN)_6 \cdot 2H_2O$ (Fig. 123). $a : b : c = 1.9855 : 1 : 1.0760$; $\alpha = 96°59'$; $\beta = 109°35'$; $\gamma = 87°11'$; $a\{100\}$, $c\{001\}$, $m\{110\}$, $r\{101\}$, $k\{011\}$.

This class probably also includes potassium dichromate, $K_2Cr_2O_7$.

2. *Pinacoidal class* (symmetry formula C) has only a centre of symmetry.

The only possible simple form is a pinacoid $\{hkl\}$, where h, k, and l can be positive or negative integers, including ± 1 and 0. This class is represented by about 650 minerals and artificial crystals.

Examples

(1) Chalcanthite (copper sulphate), $CuSO_4 \cdot 5H_2O$ (Fig. 124). $a : b : c = 0.5721 : 1 : 0.5554$; $\alpha = 82°05'$, $\beta = 107°08'$, $\gamma = 102°41'$. Fig. 124 shows a combination of eight pinacoids: $a\{100\}$, $b\{010\}$, $m\{110\}$, $M\{1\bar{1}0\}$, $h\{120\}$, $p\{1\bar{1}1\}$, $v\{021\}$, $s\{121\}$.

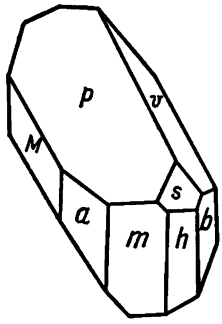


Fig. 124. Chalcanthite

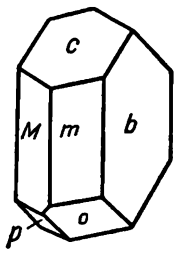


Fig. 125. Albite

(2) Albite, $NaAlSi_3O_8$ (Fig. 125). $a : b : c = 0.6335 : 1 : 0.5577$; $\alpha = 94°03'$, $\beta = 116°29'$, $\gamma = 88°09'$. Fig. 125 shows a combination of six pinacoids: $b\{010\}$, $c\{001\}$, $m\{110\}$, $M\{1\bar{1}0\}$, $o\{11\bar{1}\}$, $p\{1\bar{1}\bar{1}\}$.

Sassolin, $B(OH)_3$, also crystallizes in this class.

MONOCLINIC SYSTEM

3. *Sphenoidal class* (symmetry formula L^2) has one twofold axis (polar).

The class includes three simple forms:

(1) pedion $\{010\}$ or $\{0\bar{1}0\}$;

(2) pinacoid $\{100\}$, $\{001\}$, $\{h0l\}$; and

(3) sphenoid $\{0kl\}$, $\{hk0\}$, $\{hkl\}$ being the general form.

Enantiomorphous combinations are also possible. About 200 substances crystallize in this class.

Examples

(1) Tartaric acid, right- and left-hand varieties, $C_4H_6O_6$ (Fig. 126). $a : b : c = 1.2747 : 1 : 1.0266$; $\beta = 100°17'$. Fig. 126 shows a combination of four pinacoids: $a\{100\}$, $c\{001\}$, $r\{101\}$, and $\rho\{10\bar{1}\}$, and three sphenoids $m\{110\}$ and $\{1\bar{1}0\}$, $\mu\{1\bar{1}0\}$ and $\{110\}$, $q\{01\bar{1}\}$ and $\{0\bar{1}1\}$.

(2) Lactose (lactic sugar), $C_{12}H_{22}O_{11} \cdot H_2O$ (Fig. 127). $a : b : c = 0.3077 : 1 : 0.2143$; $\beta = 109°47'$. The forms in Fig. 127 are pedions

$b\{010\}$ and $\beta\{0\bar{1}0\}$, pinacoid $a\{100\}$ and sphenoids $m\{110\}$, $\mu\{1\bar{1}0\}$, and $q\{0\bar{1}1\}$. Only two edges of the face β are seen in Fig. 127.

Sucrose and *l*-cocaine are also included in this class.

4. *Domatic class* (symmetry formula *P*) has one plane of symmetry. Three simple forms are included in this class:

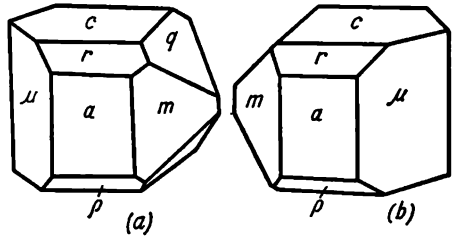


Fig. 126. Tartaric acid:
(a) right-hand variety; (b) left-hand variety

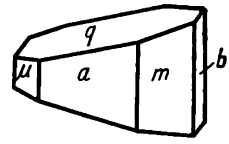


Fig. 127. Lactose

(1) pedion $\{100\}$, $\{\bar{1}00\}$, $\{001\}$, $\{00\bar{1}\}$, $\{h0l\}$;
(2) pinacoid $\{010\}$, and
(3) dome $\{0kl\}$, $\{hk0\}$, $\{hkl\}$ being the general form.
This class is represented by very few crystals.

Example

Potassium tetrathionate, $K_2S_4O_6$. $a : b : c = 0.9302 : 1 : 1.2666$; $\beta = 104°16'$. Fig. 128 shows a combination of three pedions: $a\{100\}$,

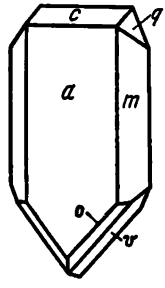


Fig. 128. Potassium tetrathionate

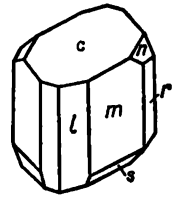


Fig. 129. Realgar

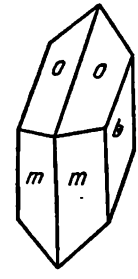


Fig. 130. Gypsum

$\alpha\{\bar{1}00\}$, and $c\{001\}$, and six domes: $m\{110\}$, $\mu\{1\bar{1}0\}$, $q\{011\}$, $v\{11\bar{3}\}$, $o\{11\bar{1}\}$, and $p\{\bar{1}1\bar{1}\}$ (forms α, μ, and p are not visible).

5. *Prismatic class* (symmetry formula L^2PC). One twofold axis and a plane perpendicular to it are characteristic with the centre of symmetry at the point of intersection of the axis and the plane.

Two simple forms make up the class:

(1) pinacoid {100}, {010}, {001}, {*h*0*l*}, and

(2) rhombic prism {0*kl*}, {*hk*0}, {*hkl*} being the general form.

All faces perpendicular or parallel to the plane of symmetry are pinacoid faces, and those intersecting the axis and the plane of symmetry at an oblique angle are rhombic prism faces.

This class embraces the greatest number of crystals (over 3,000) and is foremost among the 32 classes.

Examples

(1) Realgar, AsS (Fig. 129). $a : b : c = 1.4403 : 1 : 0.9729$; $\beta = 113°55'$. Fig. 129 shows a combination of two pinacoids: $r\{010\}$ and $c\{001\}$, and four rhombic prisms: $m\{110\}$, $l\{210\}$, $n\{011\}$, $s\{11\bar{1}\}$.

(2) Gypsum (calcium sulphate), $CaSO_4 \cdot 2H_2O$ (Fig. 130). $a : b : c = 0.6895 : 1 : 0.4132$; $\beta = 98°58'$. Fig. 130 shows a combination of a pinacoid $b\{010\}$, and two rhombic prisms: $m\{110\}$ and $o\{111\}$.

Very many minerals and other substances crystallize with a symmetry of this class, e.g., sodium bicarbonate, silicylic acid, phenacetine, sulphite, hyposulphite, red and yellow prussiates of potash, borax, dihydric oxalic acid, naphthalene.

ORTHORHOMBIC SYSTEM

6. *Rhombic tetrahedral class* (symmetry formula $3L^2$, Fig. 131), with three mutually perpendicular twofold axes.

The class includes three simple forms:

(1) pinacoid {100}, {010}, {001};

(2) rhombic prism {0*kl*}, {*h*0*l*}, {*hk*0}, and

(3) rhombic tetrahedron, right-hand {*hkl*}, and left-hand {$h\bar{k}l$}, being the general form.

About 450 substances crystallize with a symmetry of this class.

Examples

(1) Tartar emetic, $C_4H_4O_6(SbO)K \cdot H_2O$ (Fig. 132). $a : b : c = 0.9578 : 1 : 1.1048$. Fig. 132 shows a combination of a pinacoid $c\{001\}$, a rhombic prism $m\{110\}$, and two rhombic tetrahedra: right-hand $o\{111\}$, and left-hand $\omega\{1\bar{1}1\}$.

(2) Epsomite (magnesium sulphate, epsom salts), $MgSO_4 \cdot 7H_2O$. $a : b : c = 0.9901 : 1 : 0.5709$. Figure 133 shows (a) right-hand, and (b) left-hand combinations of rhombic prism $m\{110\}$ and rhombic tetrahedron $o\{111\}$ or $\omega\{1\bar{1}1\}$.

The same class includes many alkaloids—strychnine, codeine, cocaine-chloral hydrate, etc.

7. *Rhombic pyramidal class* (symmetry formula $L^2 2P$, Fig. 134). Two symmetry planes intersect along a twofold axis.

Five simple forms belong here:
(1) pedion {001}, {00$\bar{1}$};
(2) pinacoid {100}, {010};
(3) dome {0*kl*}, {*h*0*l*};
(4) rhombic prism {*hk*0}, and
(5) rhombic pyramid {*hkl*} being the general form.
Representatives of the class are few (about 50).

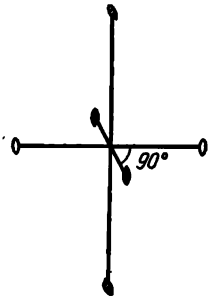


Fig. 131. Symmetry elements of the $3L^2$ class

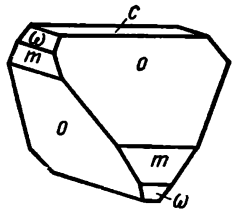


Fig. 132. Tartar emetic

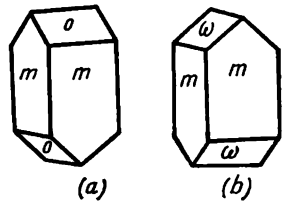


Fig. 133. Epsomite

Examples

(1) Calamine, $Zn_4(OH)_2Si_2O_7 \cdot H_2O$. $a : b : c = 0.7835 : 1 : 1.4778$. Fig. 135 shows a combination of a pedion $c\{001\}$, two pinacoids $a\{100\}$ and $b\{010\}$, a rhombic prism $m\{110\}$, four domes: $s\{301\}$, $r\{101\}$, $t\{031\}$ and $l\{011\}$, and a rhombic pyramid $q\{12\bar{1}\}$.

(2) Struvite—ammonium-magnesium phosphate, $(NH_4)MgPO_4 \cdot 6H_2O$. $a : b : c = 0.5667 : 1 : 0.9121$. Fig. 136, *a* shows a combination obtained by crystallization from an aqueous solution in the presence of $MgSO_4$: pedion $c\{001\}$, pinacoid $b\{010\}$, and domes $r\{101\}$ and $\tau\{02\bar{1}\}$.

Natural crystals of the mineral struvite appear as shown in Fig. 136, *b*: pedion $\gamma\{00\bar{1}\}$, pinacoid $b\{010\}$, and four domes: $q\{011\}$, $u\{04\bar{1}\}$, $\sigma\{10\bar{3}\}$, and $r\{101\}$ (the γ form is not visible).

Silver nitrate ($AgNO_3$) also crystallizes with the symmetry of this class

8. *Rhombic bipyramidal class* (symmetry formula $3L^23PC$, Fig. 137), with three mutually perpendicular symmetry planes intersecting along three twofold axes and a centre of symmetry.

This class has three simple forms:
(1) pinacoid {100}, {010}, {001};
(2) rhombic prism {0*kl*}, {*h*0*l*}, {*hk*0}, and
(3) rhombic bipyramid {*hkl*} being the general form.

This class is next after L^2PC in the abundance of substances (about 1,500) crystallizing with its symmetry.

It includes a great many minerals and well-known substances, such as potassium permanganate, $KMnO_4$, potassium nitrate, KNO_3, acetic acid, mercury dichloride, anhydrous oxalic acid, etc.

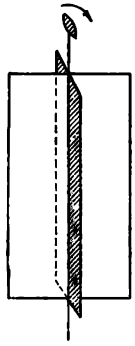


Fig. 134. Symmetry elements of the L^22P class

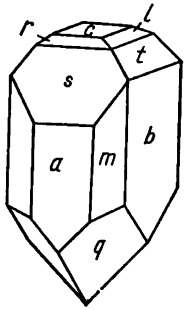


Fig. 135. Calamine

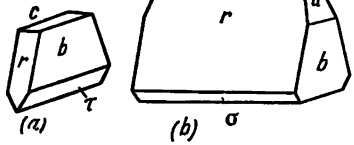


Fig. 136. Struvite

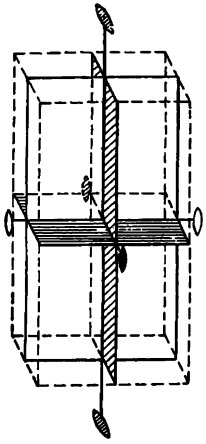


Fig. 137. Symmetry elements of the $3L^23PC$ class

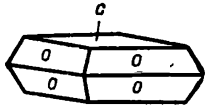


Fig. 138. Iodine

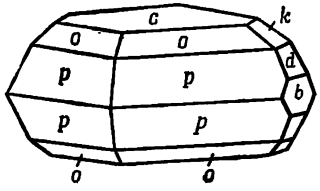


Fig. 139. Lead chloride

Examples

(1) Iodine, I. $a : b : c = 0.6644 : 1 : 1.3653$. Fig. 138 shows a combination of a pinacoid $c\{001\}$ with a rhombic bipyramid $o\{111\}$.

(2) Lead chloride, $PbCl_2$. $a : b : c = 0.5943 : 1 : 1.1898$. Fig. 139 shows a combination of pinacoids $b\{010\}$ and $c\{001\}$, two rhombic prisms $k\{012\}$ and $d\{021\}$, and two rhombic bipyramids $p\{111\}$ and $o\{112\}$.

TETRAGONAL SYSTEM

9. *Tetragonal pyramidal class* (symmetry formula L^4), with a single fourfold symmetry axis (polar).

There are three simple forms in this class:

(1) pedion {001}, {00$\bar{1}$};

(2) tetragonal prism {110}, {100}, {*hk*0}, and

(3) tetragonal pyramid {*hhl*}, {*h*0*l*}, {*hkl*} being the general form.

The class has very few representatives.

Example

Wulfenite ($PbMoO_4$). $a : c = 1 : 1.5777$. Fig. 140 shows a combination of five tetragonal pyramids: *o*{111}, ω{11$\bar{1}$}, *x*{432}, *s*{31$\bar{1}$}, and *e*{10$\bar{1}$}.

10. *Tetragonal trapezohedral class* (symmetry formula $L^4 4L^2$, Fig. 141), with a fourfold axis and four twofold axes normal to it.

Five simple forms are possible in the class:

(1) pinacoid {001};

(2) tetragonal prism {110}, {100};

(3) ditetragonal prism {*hk*0};

(4) tetragonal bipyramid {*hhl*}, {*h*0*l*}, and

(5) tetragonal trapezohedron {*hkl*} being also the general form (right- and left-hand varieties).

The class has few representatives.

Example

Potassium trichloroacetate $CCl_3(CO_2K)\cdot CCl_3(CO_2H)$. $a : c = 1 : 0.7808$. Fig. 142 shows a combination of a tetragonal bipyramid *o*{111} and a tetragonal trapezohedron *x*{311}.

11. *Tetragonal bipyramidal class* (symmetry formula L^4PC), with a fourfold symmetry axis, a plane perpendicular to it, and a centre of symmetry.

Three simple forms are possible:

(1) pinacoid {001};

(2) tetragonal prism {110}, {100}, {*hk*0}, and

(3) tetragonal bipyramid {*hhl*}, {*h*0*l*}, {*hkl*} being the general form.

The class has few representatives.

Examples

(1) Scheelite, $CaWO_4$. $a:c = 1:1.5268$. Fig. 143 shows a combination of four tetragonal bipyramids: *p*{101}, *y*{313}, *o*{111}, and *s*{131}.

(2) *i*-Erythritol, $C_4H_{10}O_4$. $a : c = 1 : 0.3762$. Fig. 144 shows a combination of a tetragonal prism *m*{100} and three tetragonal bipyramids: *o*{111}, *s*{131}, and *k*{311}.

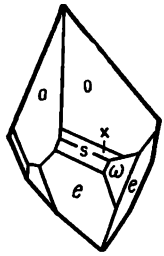


Fig. 140. Wulfenite

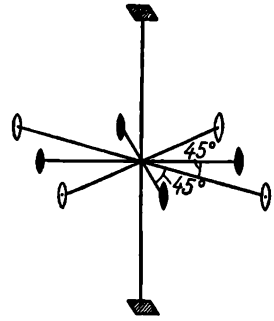


Fig. 141. Symmetry elements of the $L^4 4L^2$ class

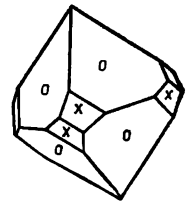


Fig. 142. Potassium trichloroacetate

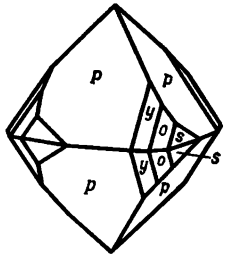


Fig. 143. Scheelite

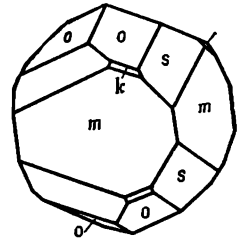


Fig. 144. *t*-Erythritol

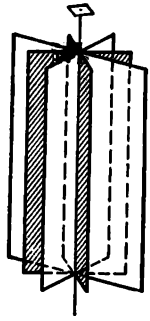


Fig. 145. Symmetry elements of the $L^4 4P$ class

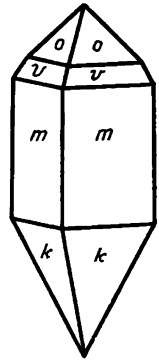


Fig. 146. Succiniodimide

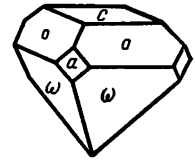


Fig. 147. Pentaerythritol

12. *Ditetragonal pyramidal class* (symmetry formula $L^4 4P$, Fig. 145). Four symmetry planes intersect in a fourfold polar axis.

Five simple forms are possible in this class:

(1) pedion {001}, {00$\bar{1}$};
(2) tetragonal prism {110}, {100};
(3) ditetragonal prism {*hk*0};
(4) tetragonal pyramid {*hhl*}, {*h*0*l*}, and
(5) ditetragonal pyramid {*hkl*} being the general form.

Very few substances crystallize with the symmetry of this class.

Examples

(1) Succiniodimide, $C_4H_4INO_2$. $a : c = 1 : 0.8733$. Fig. 146 shows a combination of a tetragonal prism $m\{110\}$ and three tetragonal pyramids: $o\{111\}$, $v\{221\}$, and $k\{22\bar{1}\}$.

(2) Pentaerythritol, $C(CH_2 \cdot OH)_4$. $a : c = 1 : 1.0236$. Fig. 147 shows a combination of a pedion $c\{001\}$, a tetragonal prism $a\{100\}$, and two tetragonal pyramids: $o\{11\bar{1}\}$, and $\omega\{11\bar{1}\}$.

13. *Ditetragonal bipyramidal class* (symmetry formula $L^4 4L^2 5PC$, Fig. 148), with one fourfold axis, four twofold axes normal to it, five planes of symmetry, and a centre of symmetry.

This class has the following five simple forms:

(1) pinacoid {001};
(2) tetragonal prism {110}, {100};
(3) ditetragonal prism {*hk*0};
(4) tetragonal bipyramid {*hhl*}, {*h*0*l*}, and
(5) ditetragonal bipyramid {*hkl*} being the general form.

This class has the largest number of substances of the tetragonal system, which is on the whole very sparingly represented.

Examples

(1) Vesuvianite, $Ca_3Al_3(OH)_4[SiO_4]_2$. $a : c = 1 : 0.535\text{-}0.5372$. Fig. 149 shows a combination of a pinacoid $c\{001\}$, tetragonal prisms $a\{100\}$ and $m\{110\}$, a ditetragonal prism $l\{210\}$ and tetragonal bipyramids $o\{111\}$ and $d\{101\}$.

(2) Cassiterite, SnO_2. $a : c = 1 : 0.6723$. Fig. 150 shows a combination of tetragonal prisms $a\{100\}$ and $m\{110\}$ and tetragonal bipyramids $o\{111\}$ and $d\{101\}$.

14. *Tetragonal tetrahedral class* (symmetry formula L_4^2), with a single rotoreflection fourfold axis.

Three simple forms are possible in this class:

(1) pinacoid {001};
(2) tetragonal prism {110}, {100}, {*hk*0}, and
(3) tetragonal tetrahedron {*hhl*}, {*h*0*l*}, and {*hkl*} being the general form.

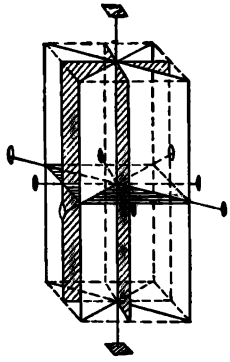


Fig. 148. Symmetry elements of the $L^4 4L^2 5PC$ class

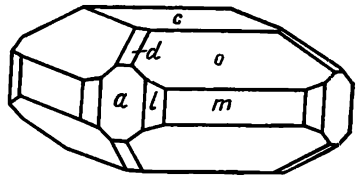


Fig. 149. Vesuvianite

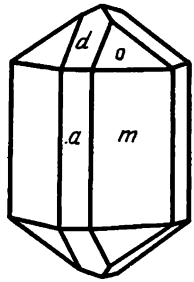


Fig. 150. Cassiterite

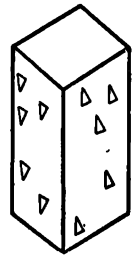


Fig. 151. Calcium alumosilicate

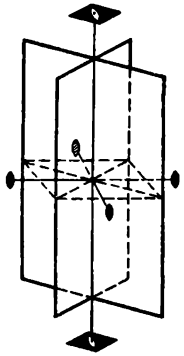


Fig. 152. Symmetry elements of the $L_4^2 2L^2 2P$ class

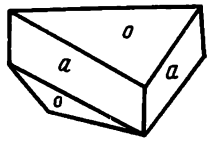


Fig. 153. Mercuric cyanide

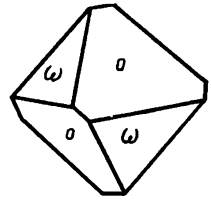


Fig. 154. Chalcopyrite

The single known representative of this class is synthetic calcium alumosilicate, discovered by S. Weiberg, which has the formula $Ca_2Al[SiAlO_7]$. Its symmetry has been established with the aid of etch figures (Fig. 151).

15. *Tetragonal scalenohedral class* (symmetry formula $L_4^2 2L^2 2P$, Fig. 152), with a fourfold rotoreflection axis, two twofold axes normal to it, and two planes of symmetry intersecting along the fourfold axis.

This class has six simple forms:
(1) pinacoid {001};
(2) tetragonal prism {110};
(3) ditetragonal prism {*hk*0};
(4) tetragonal bipyramid {*h*0*l*};
(5) tetragonal tetrahedron {*hhl*}, and
(6) tetragonal scalenohedron {*hkl*} being the general form.
This class has about 20 representatives.

Examples

(1) Mercuric cyanide, $Hg(CN)_2$. $a : c = 1 : 0.4596$. Fig. 153 shows a combination of a tetragonal prism $a\{100\}$ and a tetragonal tetrahedron $o\{111\}$.

(2) Chalcopyrite, $CuFeS_2$. $a : c = 1 : 0.9856$. Fig. 154 shows a combination of two tetragonal tetrahedra: right-hand variety $o\{111\}$, and left-hand variety $\omega\{1\bar{1}1\}$.

TRIGONAL SYSTEM

16. *Trigonal pyramidal class* (symmetry formula L^3), with a single threefold (polar) axis.

The class has three simple forms:
(1) pedion {0001}, {000$\bar{1}$};
(2) trigonal prism {10$\bar{1}$0}, {01$\bar{1}$0}, {11$\bar{2}$0}, {2$\bar{1}\bar{1}$0}, {*hik*0}, and
(3) trigonal pyramid {*h*0*h*$\bar{l}$}, {*hh*2$\bar{h}\bar{l}$}, {*hikl*} — the general form.
This class has very few representatives.

Example

Sodium iodate, $Na_2I_2O_8 \cdot 6H_2O$. $a : c = 1 : 1.094$. Fig. 155 shows a pedion $c\{000\bar{1}\}$ and trigonal pyramids $r\{10\bar{1}1\}$, $e\{02\bar{2}1\}$, and $s\{21\bar{3}1\}$. The pedion $c\{0001\}$ is not visible in Fig. 155.

17. *Trigonal trapezohedral class* (symmetry formula $L^3 3L^2$, Fig. 156), with one threefold axis and three twofold polar axes normal to it.

This class has seven simple forms:
(1) pinacoid {0001};
(2) trigonal prism {11$\bar{2}$0};

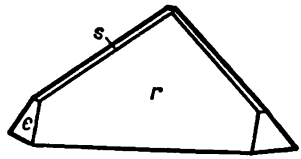


Fig. 155. Sodium iodate

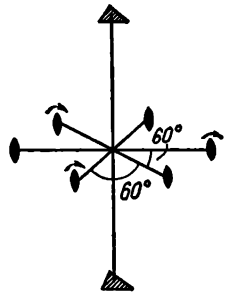


Fig. 156. Symmetry elements of the $L^3 3L^2$ class

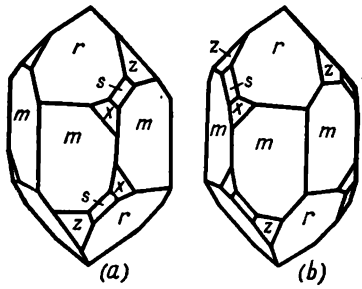


Fig. 157. Quartz:
(a) right-hand variety; (b) left-hand variety

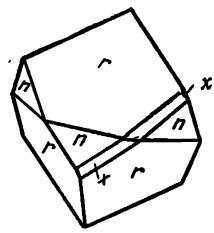


Fig. 158. Cinnabar

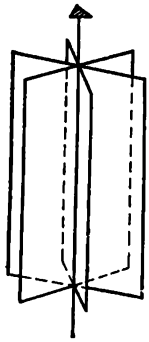


Fig. 159. Symmetry elements of the $L^3 3P$ class

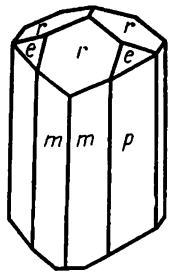


Fig. 160. Tourmaline

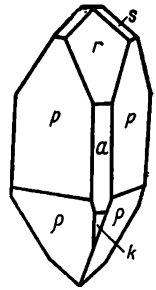


Fig. 161. Tolyl-phenyl-ketone

(3) ditrigonal prism $\{hik0\}$;
(4) hexagonal prism $\{10\bar{1}0\}$;
(5) rhombohedron $\{h0\bar{h}l\}$;
(6) trigonal bipyramid $\{hh\bar{2}hl\}$, and
(7) trigonal trapezohedron $\{hikl\}$, right- and left-hand varieties, being the general form.

This class has about 20 representatives.

Examples

(1) β-quartz, SiO_2. $a : c = 1 : 1.1000$. Fig. 157, *a* shows: a hexagonal prism $m\{10\bar{1}0\}$, rhombohedra $r\{10\bar{1}1\}$ and $z\{01\bar{1}1\}$, a trigonal bipyramid $s\{11\bar{2}1\}$ and a trigonal trapezohedron $x\{51\bar{6}1\}$. For the left-hand variety (Fig. 157, *b*) the last two forms have symbols $s\{2\bar{1}\bar{1}1\}$ and $x\{6\bar{1}\bar{5}1\}$.

(2) Mercuric sulphide (cinnabar), HgS. $a : c = 1 : 1.1453$. Fig. 158 shows rhombohedra $r\{10\bar{1}1\}$ and $n\{20\bar{2}1\}$, and a trigonal trapezohedron $x\{42\bar{6}3\}$.

18. *Ditrigonal pyramidal class* (symmetry formula $L^3 3P$, Fig. 159), with three symmetry planes intersecting along a threefold polar axis.

The class has seven simple forms:
(1) pedion $\{0001\}$, $\{000\bar{1}\}$;
(2) trigonal prism $\{10\bar{1}0\}$, $\{01\bar{1}0\}$;
(3) hexagonal prism $\{11\bar{2}0\}$;
(4) ditrigonal prism $\{hik0\}$;
(5) trigonal pyramid $\{h0\bar{h}l\}$, $\{0h\bar{h}l\}$;
(6) hexagonal pyramid $\{hh\bar{2}hl\}$, and
(7) ditrigonal pyramid $\{hikl\}$ being the general form.

Very few substances crystallize with the symmetry of this class.

Examples

(1) Tourmaline, (Na, Ca) (Mg, Fe, Li)$_6$B$_3$Al$_3$Si$_6$(O, OH)$_{30}$. $a : c = 1 : 0.4476$. Fig. 160 shows a trigonal prism $p\{01\bar{1}0\}$, a hexagonal prism $m\{11\bar{2}0\}$, and trigonal pyramids $r\{10\bar{1}1\}$, $e\{02\bar{2}1\}$, $\rho\{\bar{1}01\bar{1}\}$, and $k\{0\bar{1}12\}$. The last two forms are not visible in Fig. 160, as they bound the crystal from below.

(2) Tolyl-phenyl-ketone, $C_{14}H_{15}O$. $a : c = 1 : 1.2254$. Fig. 161 shows trigonal prisms $a\{10\bar{1}0\}$ and $p\{1\bar{1}00\}$, and trigonal pyramids $r\{10\bar{1}1\}$, $s\{01\bar{1}2\}$, $\rho\{\bar{1}01\bar{1}\}$, and $k\{0\bar{1}1\bar{1}\}$.

19. *Rhombohedral class* (symmetry formula $L_6^3 C$), with a sixfold rotoreflection axis and a centre of symmetry.

The class has three simple forms:
(1) pinacoid $\{0001\}$;
(2) hexagonal prism $\{10\bar{1}0\}$, $\{11\bar{2}0\}$, $\{hik0\}$, and
(3) rhombohedron $\{h0hl\}$, $\{hh\bar{2}hl\}$, $\{hikl\}$ being the general form.

The class has few representatives.

Examples

(1) Dioptase, $Cu_6[Si_6O_{15}]\,6H_2O$. $a : c = 1 : 0.5342$. Fig. 162 shows a hexagonal prism $a\{11\bar{2}0\}$, and rhombohedra $o\{02\bar{2}1\}$ and $u\{\bar{1}\,14\,\bar{1}\bar{3}\,6\}$.

(2) Phenacite, Be_2SiO_4. $a : c = 1 : 0.6611$. Fig. 163 shows hexagonal prisms $m\{10\bar{1}0\}$ and $a\{11\bar{2}0\}$, and rhombohedra $x\{13\bar{4}1\}$, $r\{10\bar{1}1\}$, $s\{21\bar{3}1\}$ and $d\{01\bar{1}2\}$.

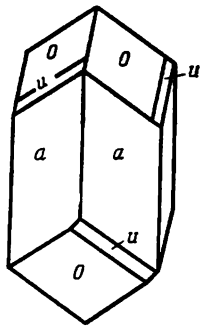


Fig. 162. Dioptase

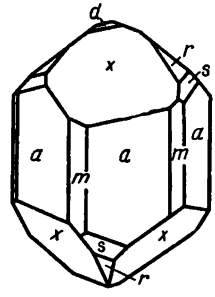


Fig. 163. Phenacite

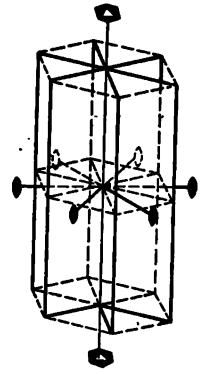


Fig. 164. Symmetry elements of $L_6^3 3L^2 3PC$ class

20. *Ditrigonal scalenohedral class* (symmetry formula $L_6^3 3L^2 3PC$, Fig. 164), with three symmetry planes intersecting along the L_6^3 axis; normal to it and at an angle of 30° to the planes are located three twofold axes; a centre of symmetry lies at the point of intersection.

The class has six simple forms:

(1) pinacoid $\{0001\}$;
(2) hexagonal prism $\{10\bar{1}0\}$, $\{11\bar{2}0\}$;
(3) dihexagonal prism $\{hik0\}$;
(4) rhombohedron $\{h0\bar{h}l\}$;
(5) hexagonal bipyramid $\{hh\bar{2}hl\}$, and
(6) ditrigonal scalenohedron $\{hikl\}$ being the general form.

This class is more richly represented than any other class of the trigonal system.

Examples

(1) Hematite, Fe_2O_3. $a : c = 1 : 1.3653$. Fig. 165 shows rhombohedra $r\{10\bar{1}1\}$ and $e\{01\bar{1}4\}$, and a hexagonal bipyramid $n\{22\bar{4}3\}$. The latter may easily be mistaken for a scalenohedron, the difference being in the position of the edges between the upper and the lower

faces. If the edges along which the upper and the lower faces intersect are perpendicular to L_6^3, the form is a bipyramid, if they are inclined to the axis, the form is a scalenohedron.

(2) Calcite, $CaCO_3$. $a : c = 1 : 0.8543$. Fig. 166 shows a hexagonal prism $a\{11\bar{2}0\}$ and a ditrigonal scalenohedron $s\{21\bar{3}1\}$.

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21. *Trigonal bipyramidal class* (symmetry formula L^3P), with a threefold axis and a symmetry plane normal to it.

The class has three simple forms:

(1) pinacoid $\{0001\}$;

(2) trigonal prism $\{10\bar{1}0\}$, $\{01\bar{1}0\}$, $\{11\bar{2}0\}$, $\{2\bar{1}10\}$, and

(3) trigonal bipyramid $\{h0\bar{h}l\}$, $\{hh\bar{2}\bar{h}l\}$, $\{hikl\}$ being the general form.

Example

Only one substance, and even that not thoroughly studied crystallographically, has been assigned to this class: silver phosphate, Ag_2HPO_4. $a : c = 1 : 0.7297$. Fig. 167 shows trigonal prisms $m\{10\bar{1}0\}$, $\mu\{0\bar{1}10\}$, and trigonal bipyramids $r\{10\bar{1}1\}$, $s\{02\bar{2}1\}$, and $\sigma\{20\bar{2}1\}$.

22. *Ditrigonal bipyramidal class* (symmetry formula L^33L^24P, Fig. 168), with a threefold axis, three twofold axes, and four symmetry planes.

This class has seven simple forms:

(1) pinacoid $\{0001\}$;

(2) trigonal prism $\{10\bar{1}0\}$, $\{01\bar{1}0\}$;

(3) hexagonal prism $\{11\bar{2}0\}$;

(4) ditrigonal prism $\{hik0\}$;

(5) trigonal bipyramid $\{h0\bar{h}l\}$ and $\{0h\bar{h}l\}$;

(6) hexagonal bipyramid $\{hh\bar{2}\bar{h}l\}$, and

(7) ditrigonal bipyramid $\{hikl\}$ being the general form.

Example

The only representative (and even that not quite certain) of this class is the mineral benitoite, $BaTiSi_3O_9$. $a : c = 1 : 0.7319$. Fig. 169 shows a pinacoid $c\{0001\}$, trigonal prisms $m\{10\bar{1}0\}$, $M\{01\bar{1}0\}$, and trigonal bipyramids $r\{10\bar{1}1\}$ and $p\{01\bar{1}1\}$.

23. *Hexagonal pyramidal class* (symmetry formula L^6), with a single sixfold axis (polar).

The class has three simple forms:

(1) pedion $\{0001\}$, $\{000\bar{1}\}$;

(2) hexagonal prism $\{10\bar{1}0\}$, $\{11\bar{2}0\}$, $\{hik0\}$, and

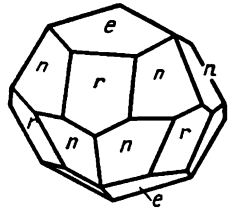

Fig. 165. Hematite

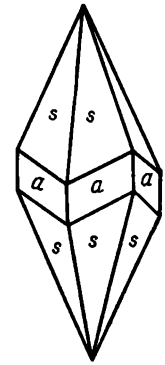

Fig. 166. Calcite

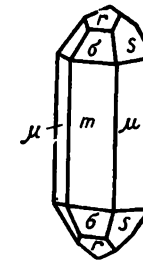

Fig. 167. Silver phosphate

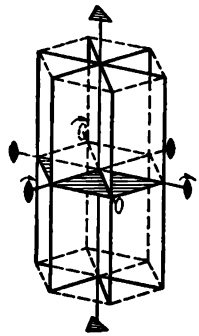

Fig. 168. Symmetry elements of the $L^3 3L^2 4P$ class

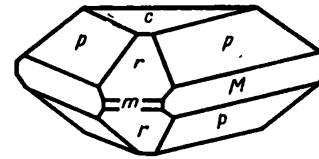

Fig. 169. Benitoite

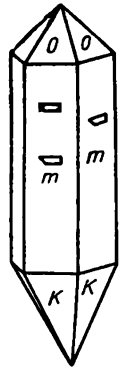

Fig. 170. Strontium antimonyl tartrate

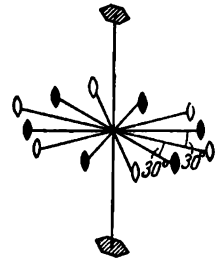

Fig. 171. Symmetry elements of the $L^6 6L^3$ class

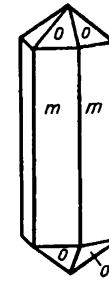

Fig. 172. Potassium silicomolybdate

(3) hexagonal pyramid $\{h0\bar{h}l\}$, $\{hh\bar{2}hl\}$, $\{hikl\}$ being the general form.

There are few representatives of this class.

Example

Strontium antimonyl tartrate, $Sr(SbO)_2(C_4H_4O_6)_2$. $a : c = 1 : 0.8442$. Fig. 170 shows a hexagonal prism $m\{10\bar{1}0\}$ and hexagonal pyramids $o\{10\bar{1}1\}$ and $k\{20\bar{2}1\}$. Etch figures confirm that the compound belongs to this class.

24. *Hexagonal trapezohedral class* (symmetry formula L^66L^2, Fig. 171), with a sixfold axis and six twofold axes normal to it.

The class has five simple forms:

(1) pinacoid $\{0001\}$;

(2) hexagonal prism $\{10\bar{1}0\}$, $\{11\bar{2}0\}$;

(3) dihexagonal prism $\{hik0\}$;

(4) hexagonal bipyramid $\{h0\bar{h}l\}$, and

(5) hexagonal trapezohedron $\{hikl\}$ being the general form.

There are few representatives of this class.

Example

Potassium silicomolybdate, $K_4Mo_{12}SiO_{40} \cdot 18H_2O$. $a : c = 1 : 0.6809$. Fig. 172 shows a hexagonal prism $m\{10\bar{1}0\}$ and a hexagonal bipyramid $o\{10\bar{1}1\}$. Etch figures confirm that the compound belongs to this class.

25. *Hexagonal bipyramidal class* (symmetry formula L^6PC), with a sixfold symmetry axis and a symmetry plane normal to it; a centre of symmetry lies at the point of their intersection.

The class has three simple forms:

(1) pinacoid $\{0001\}$;

(2) hexagonal prism $\{10\bar{1}0\}$, $\{11\bar{2}1\}$, $\{hik0\}$, and

(3) hexagonal bipyramid $\{h0\bar{h}l\}$, $\{hh\bar{2}hl\}$, $\{hikl\}$ being the general form.

This class has few representatives.

Example

Apatite, $Ca_5(Cl, F, OH)(PO_4)_3$. $a : c = 1 : 0.7356$. Fig. 173 shows a pinacoid $c\{0001\}$, hexagonal prisms $m\{10\bar{1}0\}$, $a\{11\bar{2}0\}$, and hexagonal bipyramids: $o\{10\bar{1}1\}$, $s\{11\bar{2}1\}$, $x\{3\bar{2}\bar{1}1\}$, and $t\{20\bar{2}1\}$.

26. *Dihexagonal pyramidal class* (symmetry formula L^66P, Fig. 174), with a polar sixfold axis and six symmetry planes intersecting along it.

The class has five simple forms:

(1) pedion $\{0001\}$, $\{000\bar{1}\}$;

(2) hexagonal prism $\{10\bar{1}0\}$, $\{11\bar{2}0\}$;
(3) dihexagonal prism $\{hik0\}$;
(4) hexagonal pyramid $\{h0\bar{h}l\}$, $\{hh\bar{2}\bar{h}l\}$, and
(5) dihexagonal pyramid $\{hikl\}$ being the general form.
There are few representatives of this class.

Examples

(1) Greenockite, CdS. $a : c = 1 : 1.6218$. Fig. 175 shows pedions $c\{0001\}$ and $\gamma\{000\bar{1}\}$, a hexagonal prism $m\{10\bar{1}0\}$, and hexagonal pyramids: $o\{20\bar{2}1\}$, $i\{10\bar{1}1\}$, $r\{10\bar{1}2\}$, and $\omega\{10\bar{1}\bar{1}\}$; the γ form is not visible here.

(2) Iodyrite, AgI. $a : c = 1 : 0.8196$. Fig. 176 shows a pedion $c\{0001\}$, a hexagonal prism $a\{11\bar{2}0\}$, and hexagonal pyramids $u\{40\bar{4}1\}$, $k\{40\bar{4}\bar{5}\}$, and $s\{20\bar{2}\bar{3}\}$.

27. *Dihexagonal bipyramidal class* (symmetry formula $L^6 6L^2 7PC$, Fig. 177), with a sixfold axis, six twofold axes normal to it, seven symmetry planes, and a centre of symmetry.

The class has five simple forms:
(1) pinacoid $\{0001\}$;
(2) hexagonal prism $\{10\bar{1}0\}$, $\{11\bar{2}0\}$;
(3) dihexagonal prism $\{hik0\}$;
(4) hexagonal bipyramid $\{h0\bar{h}l\}$, $\{hh\bar{2}\bar{h}l\}$, and
(5) dihexagonal bipyramid $\{hikl\}$ being the general form.
This class has more representatives than any other class of the hexagonal system.

Examples

(1) Beryl, $Be_3Al_2Si_6O_{18}$. $a : c = 1 : 0.4989$. Fig. 178 shows a pinacoid $c\{0001\}$, a hexagonal prism $m\{10\bar{1}0\}$, hexagonal bipyramids: $o\{10\bar{1}1\}$, $t\{20\bar{2}1\}$, and $r\{11\bar{2}1\}$, and a dihexagonal bipyramid $x\{32\bar{1}1\}$.

(2) Iodoform, CHI_3. $a : c = 1 : 1.1084$. Fig. 179 shows a pinacoid $c\{0001\}$, hexagonal prisms $m\{10\bar{1}0\}$ and $a\{11\bar{2}0\}$, and a hexagonal bipyramid $o\{10\bar{1}1\}$.

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28. *Tritetrahedral class* (symmetry formula $3L^2 4L^3$, Fig. 180), with three twofold axes and four (polar) threefold axes.

The class has seven simple forms (as have all classes of the cubic system):
(1) cube $\{100\}$;
(2) rhombic dodecahedron $\{110\}$;
(3) pentagonal dodecahedron $\{hk0\}$, $\{kh0\}$*;

* The adopted relationship of indices in the symbols of simple forms of the cubic system is $h > k > l$.

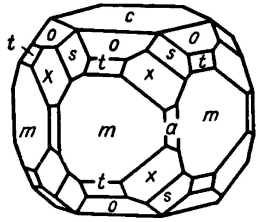


Fig. 173. Apatite

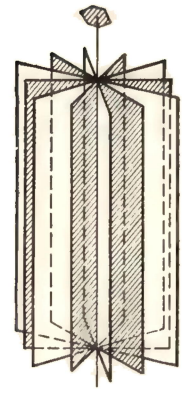


Fig. 174. Symmetry elements of the $L^6 6P$ class

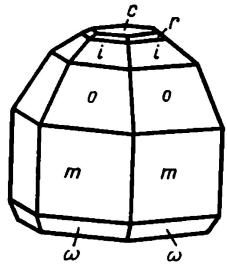


Fig. 175. Greenockite

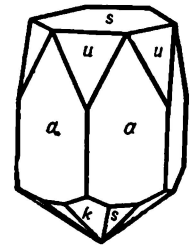


Fig. 176. Iodyrite

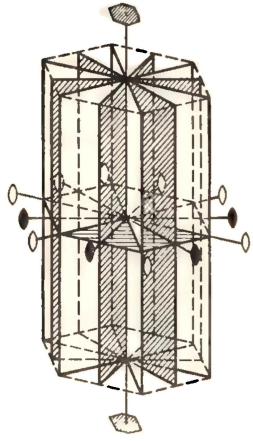


Fig. 177. Symmetry elements of the $L^6 6 L^2 7 PC$ class

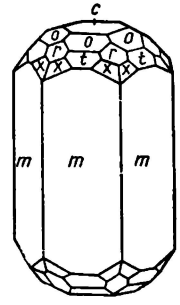


Fig. 178. Beryl

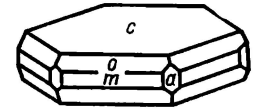


Fig. 179. Iodoform

(4) tetrahedron {111}, {1$\bar{1}$1};
(5) trigonal tritetrahedron {*hkk*}, {*hk*$\bar{k}$};
(6) tetragonal tritetrahedron {*hhl*}, {*hh*$\bar{l}$}, and
(7) pentagonal tritetrahedron, right-hand variety {*khl*} and left-hand variety {*hkl*} being the general form.

Examples

(1) Lead nitrate, $Pb(NO_3)_2$. Fig. 181 shows a pentagonal tritetrahedron *s*{10 5 6} and tetrahedra *o*{111} and ω{1$\bar{1}$1}.

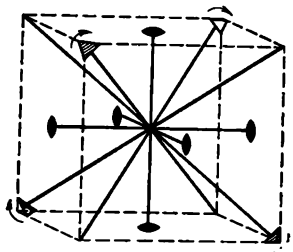


Fig. 180. Symmetry elements of the $3L^24L^3$ class

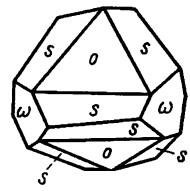


Fig. 181. Lead nitrate

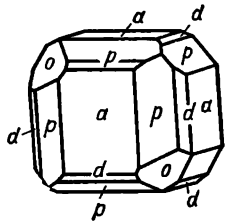


Fig. 182. Sodium chlorate

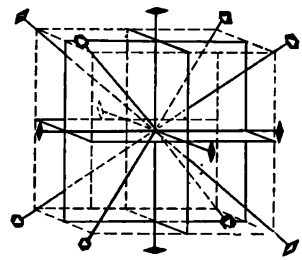


Fig. 183. Symmetry elements of the $3L^24L_6^33PC$ class

(2) Sodium chlorate, $NaClO_3$. Fig. 182 shows a cube *a*{100}, a pentagonal dodecahedron *p*{201}, a rhombic dodecahedron *d*{110}, and a tetrahedron *o*{1$\bar{1}$1}.

29. *Didodecahedral class* (symmetry formula $3L^24L_6^33PC$, Fig. 183). Addition of planes normal to twofold axes produces a centre of symmetry. The threefold axes become sixfold rotoreflection axes.

The class has seven simple forms:

(1) cube {100};

(2) rhombic dodecahedron {110};
(3) pentagonal dodecahedron {*hk*0} and {*h*0*k*};
(4) octahedron {111};
(5) tetragonal trioctahedron {*hkk*};
(6) trigonal trioctahedron {*hhk*}, and
(7) didodecahedron {*hkl*}, {*hlk*}* being the general form.

Examples

(1) Pyrite, FeS_2. Fig. 184 shows an octahedron *o*{111} and a pentagonal dodecahedron *p*{210}. This combination has been named a *mineral icosahedron* (twenty-faceted).

(2) Cobaltite, CoAsS. Fig. 185 shows a cube *a*{100}, an octahedron *o*{111}, and pentagonal dodecahedra *p*{210} and *q*{410}.

30. *Hexatetrahedral class* (symmetry formula $3L_4^2L^36P$, Fig. 186). The threefold axes are polar, symmetry planes inclined at 45° to the twofold axes turn these axes into fourfold rotoreflection axes.

This class has the following simple forms:
(1) cube {100};
(2) rhombic dodecahedron {110};
(3) tetrahexahedron {*hk*0};
(4) tetrahedron {111}, {$1\bar{1}1$};
(5) trigonal tritetrahedron {*hkk*}, {$h\bar{k}k$};
(6) tetragonal tritetrahedron {*hhl*}, {$h\bar{h}l$}, and
(7) hexatetrahedron {*hkl*}, and {$h\bar{k}l$} being the general form.

Examples

(1) Sphalerite (zinc blende), ZnS. Fig. 187 shows a cube *a*{100}, a rhombic dodecahedron *d*{110}, tetrahedra *o*{111}, and ω{$1\bar{1}1$}, and trigonal tritetrahedra *k*{311} and *i*{$2\bar{1}1$}.

(2) Tetrahedrite, $Cu_8(SbAs)_2S_7$. Fig. 188 shows a rhombic dodecahedron *d*{110}, a tetrahedron *o*{111}, and a trigonal tritetrahedron *i*{211}.

31. *Trioctahedral class* (symmetry formula $3L^44L^36L^2$, Fig. 189), with three fourfold axes, four threefold axes, and six twofold axes, without a centre or planes of symmetry.

This class has the following simple forms:
(1) cube {100};
(2) rhombic dodecahedron {110};
(3) tetrahexahedron {*hk*0};
(4) octahedron {111};
(5) tetragonal trioctahedron {*hkk*};

* In two different positions.

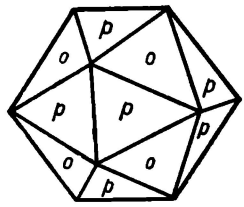


Fig. 184. Pyrite

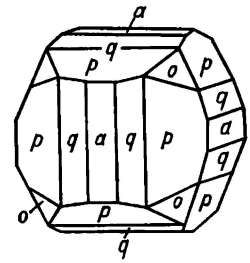


Fig. 185. Cobaltite

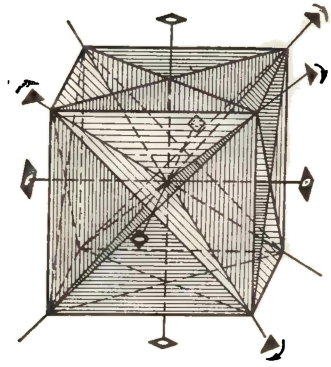


Fig. 186. Symmetry elements of the $3L_4^2 4L^3 6P$ class

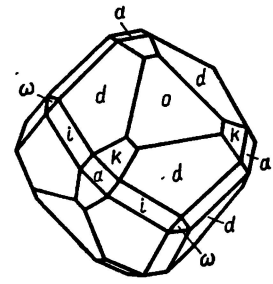


Fig. 187. Sphalerite

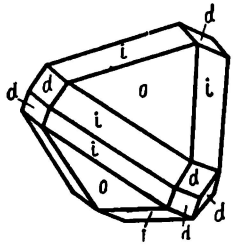


Fig. 188. Tetrahedrite

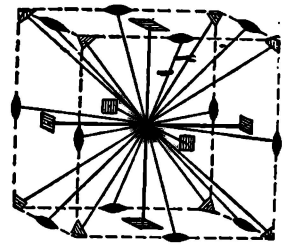


Fig. 189. Symmetry elements of the $3L^4 4L^3 6L^2$ class

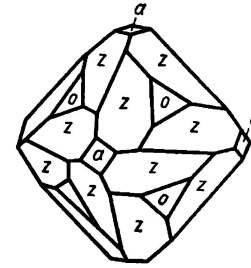


Fig. 190. Cuprite

(6) trigonal trioctahedron {*hhl*}, and
(7) pentagonal trioctahedron, right-hand variety {*hlk*} and left-hand variety {*hkl*}, being the general form.

Examples

(1) Cuprite (copper oxide), Cu_2O. Fig. 190 shows a combination of cube *a*{100}, an octahedron *o*{111}, and a pentagonal trioctahedron *z*{968}.
(2) Ammonium chloride, NH_4Cl. Fig. 191 shows a combination of a tetragonal trioctahedron *i*{211} and a pentagonal trioctahedron *x*{875}.

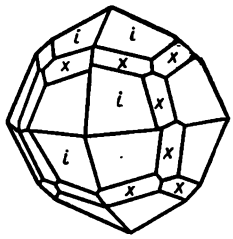


Fig. 191. Ammonium chloride

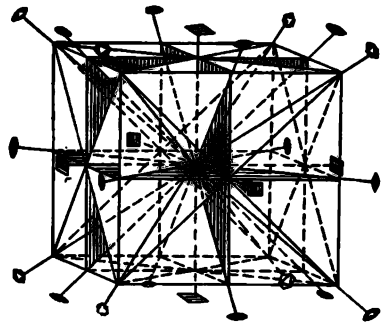


Fig. 192. Symmetry elements of the $3L^4 4L_6^3 6L^2 9PC$ class

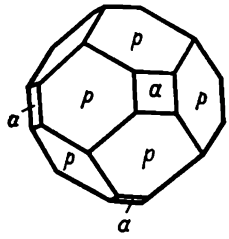


Fig. 193. Copper

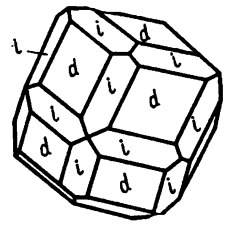


Fig. 194. Grossularite

32. *Hexoctahedral class* (symmetry formula $3L^4 4L_6^3 6L^2 9PC$, Fig. 192). Nine planes of symmetry are added to the complement of the preceding class. A centre of symmetry appears at the point of intersection, and the threefold axes become sixfold rotoreflection axes.

The class has the following simple forms:
(1) cube {100};
(2) rhombic dodecahedron {110};
(3) tetrahexahedron {*hk*0};
(4) octahedron {111};
(5) tetragonal trioctahedron {*hkk*};
(6) trigonal trioctahedron {*hhl*}; and
(7) hexoctahedron {*hkl*} being the general form.

Examples

(1) Copper, Cu. Fig. 193 shows a cube *a*{100}, and a rhombic dodecahedron *d*{110}.

(2) Grossularite, $Ca_3Al_2(SiO_4)_3$—a mineral of the garnet group. Fig. 194 shows a rhombic dodecahedron *d*{110} and a tetragonal trioctahedron *i*{211}.

CHAPTER XI

Habit and Features of Real Crystals. Twins

In the preceding pages we have studied crystal polyhedra of growth in their ideal development. Real crystals develop these forms only exceptionally and usually reveal an apparently much lower symmetry. Thus, some crystals in the cubic system, which under ideal conditions of growth should crystallize in the form of a cube, actually develop into rectangular parallelepipeds with the $3L^2 3PC$ symmetry. Quartz crystals often develop in a form which appears to belong to the triclinic pedial class L^1 instead of the trigonal trapezohedral, because the symmetry of the environment of the crystal during its growth was lower than that of the crystal itself.

Let us look at some of the most characteristic forms observed among real crystals, which differ greatly from ideal ones.

Twisted Crystals. Crystals sometimes split in the course of growth, the reason for this being still unknown. Splitting may be due to foreign matter in the melt, the rapid growth or large size of the crystal, temperature variations, and mechanical damage. Splitting results in peculiar twisted forms (Fig. 195).

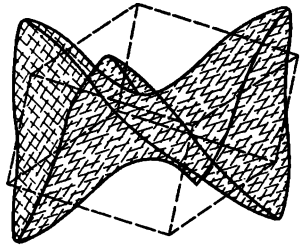


Fig. 195. Twisted crystal of siderite

Spherolites. When a melt crystallizes rapidly at one or more points, there often develop aggregates consisting of thin needle-shaped crystals radiating in the form of a sphere, the reason for such spherolitic development probably being orthotropism or a tendency towards growth in a direction perpendicular to the plane or line of crystal nucleation.

Acicular Habit. Crystals often develop in the form of needles. This is especially queer in the case of substances crystallizing in the cubic system, but examples of this are very numerous (gold, potassium chloride, etc.). The direction of needle growth coincides neither with the line of action of gravity, nor with the direction of concentration currents.

Vicinal Formations. The faces of real crystals are never ideally plane. In some cases they have small irregular depressions which are called *vicinaloids*. Sometimes these depressions form several larger sections—*vicinals* proper (from the Latin word *vicinus*—neighbour), which, in turn, have vicinaloids. There also occur curved faces. But in some cases very strong and distinct reflections (signals) are obtained on a goniometer. Examples of this are octahedron faces on spinel crystals, small bipyramid faces on beryl and topaz crystals. Sometimes the irregularities and vicinals are so large that they are visible to the naked eye. In such cases the faces produce no distinct signals

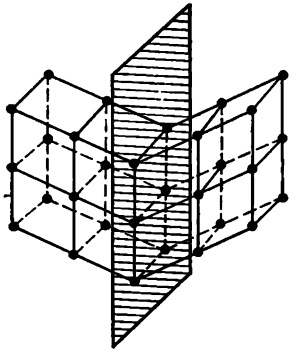


Fig. 196. Structure of the composition plane of a twin crystal

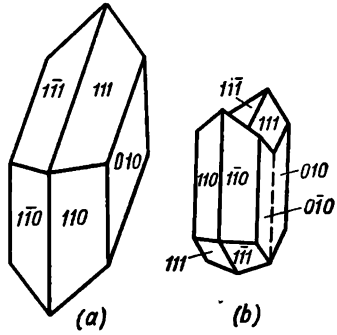


Fig. 197. Twinning about an axis (gypsum)

in a goniometer, thus making the process of establishing their symbols very complex. For instance the faces of the zone {0001} of tourmaline sometimes consist of continuous small vicinals which merge with each other at a slight angle, thus making the prism zone appear rounded.

As far as the nature of vicinal formations is concerned, some authors regard them as faces of a simple symbol displaced from their normal position in the course of crystal formation. This is probably true of vicinaloids, but not of vicinals, because their presence on some crystals is too regular to be the result of accidental displacement. For instance, an octahedral face of large crystals of potassium aluminium sulphate is, strictly speaking, never a true (111) face: it consists of three separate faces of a trigonal trioctahedron sometimes with an area reaching several square centimetres.

Twins. Well formed individual crystals can be obtained with the aid of special, sometimes rather intricate devices. Any melt or solution will usually produce crystals in the form of intergrowths. Under

natural conditions individual crystals develop rather rarely, while intergrowths are the most common result of crystallization.

Regular intergrowths of crystals of the same substance are called *twins*, these occurring when an important face of a crystal, called a *composition plane*, is superimposed on a similar face of another crystal of the same substance in a parallel but inverted position. In this case the loops of plane nets of the two faces should coincide (Fig. 196). The parallelograms of the two nets, and the two individuals of the twin can be placed in a congruent position by three symmetry operations: (1) rotation through 180° about the direction normal to the plane net, which will result in twinning about an axis (so-called twin axis) (Fig. 197); (2) reflection through a plane net as through a symmetry plane, which will result in twinning about a plane (twin plane) (Fig. 198); (3) inversion, which is possible because each parallelogram of a plane net has a centre of symmetry. In the second and third cases individual crystals constituting a twin can be right- and left-hand, i.e., each can have a different sign.

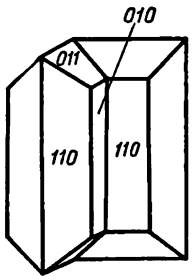


Fig. 198. Twinning about a plane (aragonite)

A twin plane is never parallel to a symmetry plane of a single crystal, as such parallelism would produce parallel intergrowth, but not a twin. In the same way the direction of a twin axis cannot be parallel to the direction of an even symmetry axis of a single crystal. A real or a possible face of a single crystal will always be the twin plane, and a real or a possible edge of a crystal—the twin axis. Externally twins can usually be distinguished by their re-entrant angles, although this feature is not necessarily present in all cases of twinning.

There are frequent cases of multiple twinning. Such intergrowths are called *trillings*, *fourlings*, depending on the number of intergrown crystals, and *polysynthetic twins* when the number of individual crystals is infinite. These twins show very characteristic alternate extinction under the microscope, i.e., darkening of very fine parallel plates.

Five cases of twin formation are known:

(1) by intergrowth of small crystals after their accidental contact during growth in a position conducive to twinning;

(2) by parallel superposition of molecules on a twin nucleus which has sprung up from two or more molecules;

(3) by superposition of molecules in a twinned position on a large crystal;

(4) by transition of one crystallographic modification into another (polymorphous transformation, e.g., of quartz);

(5) under the influence of mechanical factors.

Sometimes twins have a symmetry higher or lower than single crystals, which is otherwise known as pseudosymmetry. Some twinned crystals of the cubic system may have a sixfold symmetry axis which can never be present in single crystals of this system.

Below common types of twins in the different crystal systems are given.

Cubic system. If two octahedra intergrow on a plane parallel to one of their faces, a threefold symmetry axis will then be a twin axis, twins formed under this law are usually called spinel twins (after the mineral spinel, whose crystals occur in the form of such twins). The same law operates in the case of two intergrown cubes with a common threefold axis (twin axis), when one crystal is turned by 180° with respect to the other. Then the L_6^3 axis becomes an L^6 axis. Such twins often occur on fluorspar, CaF_2 (Fig. 199).

Tetragonal system. Crystals of rutile (TiO_2) sometimes occur in the form of twinned pyramids (Fig. 200). Sometimes these twins consist of eight crystals and have the peculiar form of a closed ring (Fig. 201).

Trigonal system. Of special interest are three types of quartz twins: (1) two crystals with the same rotation (both right-handed or both left-handed) are intergrown so that their threefold axes are parallel, but at the same time one crystal is turned by 180° with respect to the other about the L^3 axis (the Dauphiné twin, Fig. 202); (2) two crystals of different rotation (right-handed and left-handed) are intergrown so that their threefold axes are parallel and the face $(11\bar{2}0)$ is the twin plane (the Brazil twin, Fig. 203); (3) two crystals are intergrown on the face $(11\bar{2}2)$, which is the twin plane, and produce geniculate forms (the Japan twin, Fig. 204).

Monoclinic system. Three types of orthoclase twins are noteworthy, in which: (1) the face (010) is the twin plane, the twin axis is parallel to the edges of the vertical zone (the Karlsbad twin, Fig. 205); (2) the face (001) (in these cases usually well developed) is the twin plane, one individual is turned by 180° with respect to the other about a normal to the twin plane (the Manebach twin, Fig. 206); (3) the face (021) is the twin plane, and one individual is turned with respect to the other by 180° about a normal to the twin plane (the Baveno twin, Fig. 207).

Triclinic system. There are two characteristic types of twinning: (1) intergrowth on the face (010) with rotation through 180° about a nor-

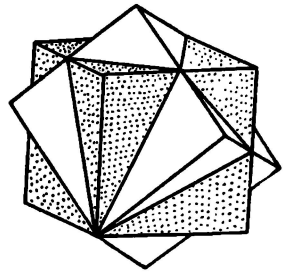


Fig. 199. Spinel twin (fluorspar)

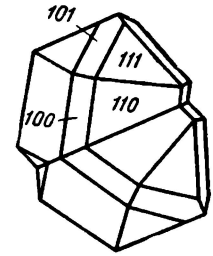


Fig. 200. A rutile twin

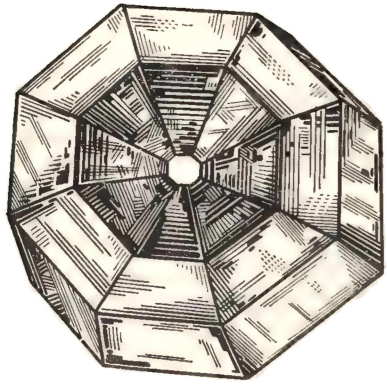


Fig. 201. A ring-shaped rutile twin

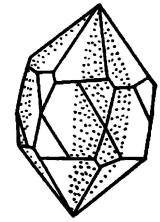


Fig. 202. Dauphiné twin

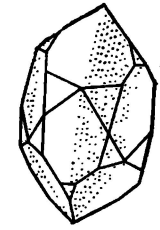


Fig. 203. Brazil twin

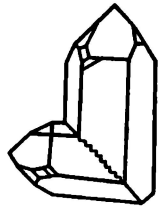


Fig. 204. Japan twin

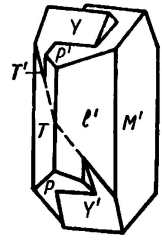


Fig. 205. Karlsbad twin

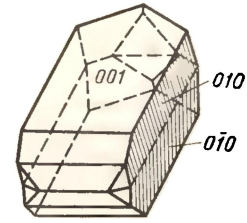


Fig. 206. Manebach twin

mal to this face (the albite twin, Fig. 208); (2) rotation through 180° occurs about the axis which lies in the plane (001) and is normal to the edge between the faces (001) and (010) (the pericline twin).

Many crystalline substances quite often crystallize in the form of twins.

Some of them occur but rarely as single crystals.

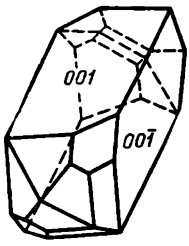


Fig. 207. Baveno twin

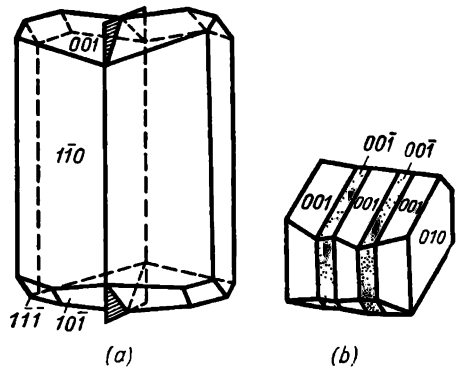


Fig. 208. Albite twin:
(a) albite twin; (b) a polysynthetic twin

Regular Intergrowths. These phenomena appear not only in crystals of the same substance but can also be found in crystals of substances similar in chemical composition and form (so-called isomorphous substances, see page 178), or in form only. As distinct from twins, regular intergrowths are composite crystals of different substances. We shall discuss a few examples of such formations.

1. Sulphates known under the collective name of alum have the following composition: $R_2SO_4 \cdot R_2'''(SO_4)_3 \cdot 24H_2O$, where $R' = K$, NH_4, Rb, Cs, while $R''' = Al$, Cr. If an alum crystal of one composition is placed in a supersaturated solution of another kind of alum it will continue to grow as if it were in a solution of alum of the first composition. The different degrees of solubility should be taken into consideration, of course. By varying the temperature and concentration, a layered crystal can be obtained, with different layers having different chemical composition.

Many such instances could be cited both among natural and artificial compounds.

2. A different case is the growth of Chile nitre, $NaNO_3$, on calcite, $CaCO_3$. In a supersaturated solution of sodium nitrate a calcite crystal can serve as a nucleus for large crystals of nitre almost as well as

a crystal of nitre itself. Here we have a case of harmonious crystallization of two substances of entirely different composition, but with closely similar interfacial angles (isogonism).

3. The third type of regular intergrowths is observed in the case of mica (muscovite) and potassium iodide, KI. The composition and form of the two substances are entirely different. But one of the mica crystal faces—the pinacoid (0001)*—is similar in the surface arran-

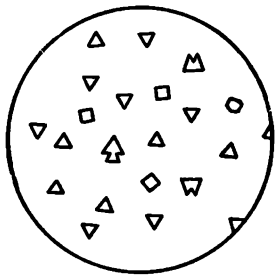


Fig. 209. Crystallization of potassium iodide on muscovite

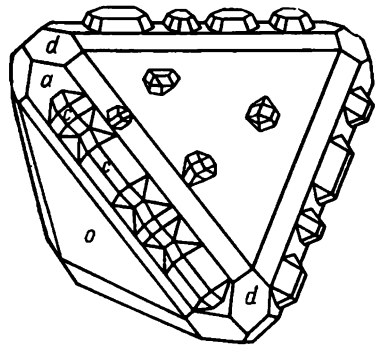


Fig. 210. Crystallization of chalcopyrite on tetrahedrite

gement of particles (as regards plane angles and distances between particles) to the face (111) of potassium iodide. If a drop of saturated solution of potassium iodide is placed on a freshly separated lamina of a muscovite crystal, the following can be observed under the microscope. Crystals of potassium iodide—usually combinations of octahedra and cubes—begin to appear on the surface of the drop as a result of evaporation of the solvent. If these crystals contact the surface of mica with their cube faces, no regular arrangement will result, but when the potassium iodide crystals contact the mica surface with their octahedron faces, they adhere to it with a definite orientation which is retained in further growth (Fig. 209).

A similar phenomenon can be observed in tetrahedrite and copper pyrites (Fig. 210).

* When regarded as pseudohexagonal.

CHAPTER XII

Crystal Structure

SPACE LATTICE

It has been mentioned several times that the space lattice constitutes the pattern of the internal structure of crystalline substances. We visualize the space lattice as an infinite geometrical image which can be built between four given points in space so that no more than two of the points should lie in one line, and no more than three of the points in one plane.

By taking four points O, A, B, C, not lying in one plane (Fig. 211), we can easily build a lattice by parallel translations of the rows a_1a_2, b_1b_2, c_1c_2 obtained between the points taken. The space lattice is constructed of points, but it can also be visualized as a combination of equal parallelepipeds continuously filling a space.

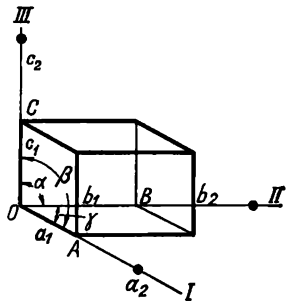


Fig. 211. Construction of a lattice from constants

As was said in Chapter I, the points of a lattice are called *nodes*, the straight lines—*rows*, the planes—*nets* (plane nets), and the parallelepipeds—*cells*. The direction and the nature of a row are defined by two neighbouring points in it. The distance between these points is called *row spacing*. All parallel rows have similar spacings, all parallel nets have similar loops in the form of parallelograms. A row is defined by the value a of its spacing, a plane net by the spacings a and b of two rows in it and by the angle of their intersection (α, β, or γ, Fig. 212).

The direct relationship between the basic tetrahedron discussed in Chapter VII and the cell of a space lattice is easily established. The initial faces (100), (010), and (001) are the three basic faces of an elementary parallelepiped (see Fig. 212), and the unit face (111) is its diagonal plane. Therefore, the choice of the axes *I*, *II*, and *III* and of the unit face fully defines the shape of the cell of the lattice which determines the structure of a given crystalline substance.

One and the same plane net can be built of most diverse parallelograms (Fig. 213), but the number and the area of the parallelograms will remain constant for this lattice. This is also true of a three-dimensional structure—a space lattice. The constant values in it are the number of parallelepipeds per unit volume, the sum of face areas, and the volume of cells, irrespective of their form.

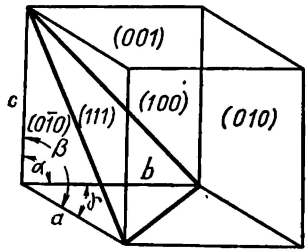


Fig. 212. A basic tetrahedron and a unit cell

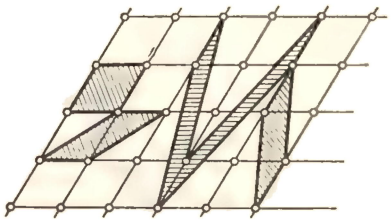


Fig. 213. Construction of a plane net

In all the above cases the nodes of a lattice should be located only at the apexes of the parallelograms of plane nets and at apexes of the solid angles of parallelepipeds, but not on the sides or inside the parallelograms or cells.

SYMMETRY OPERATIONS FOR IMAGES OF INFINITE EXTENSION

Operations with images of infinite extension should be added to the symmetry transformations discussed. Let us review the following cases.

1. Translation. Any space lattice can be placed into a position congruent with its initial position by translating it parallel to itself by one or more spacings of any of its rows. Belov regards the space lattice as an element of symmetry for the operation of translation. One cannot but agree with this.

Translation can be combined with rotation and mirror reflection, this giving two more symmetry operations.

2. Translation Combined with Rotation (Screw Axis of Symmetry). The point a_1 (Fig. 214) after rotation through 90° and translation over a distance k along the axis will move to the point a_2. By repeating the operation we obtain points a_3, a_4, a_5, etc. The point a_5 can be moved into a position congruent with a_1—the initial point—by a single translation through four row spacings (intercept T). The axis A is a fourfold screw axis, as its elementary angle of rotation is 90°.

Thus, a *screw axis of symmetry* is that direction progressing along which a figure can arrive at a congruent position by rotation combined with translation.

The rotation can be right- and left-handed, so that screw axes of the same order can also be right- and left-handed.

The screw axes have the same designations as the simple symmetry axes, i.e., L^1, L^2, L^3, L^4, L^6, but for the addition of a dot over the letter L ($\dot{L}^1$, $\dot{L}^2$, etc.). The right-handed screw axes are denoted by a plus sign before the L, and the left-handed screw axes by a minus sign.

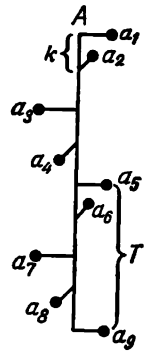


Fig. 214. A fourfold screw axis

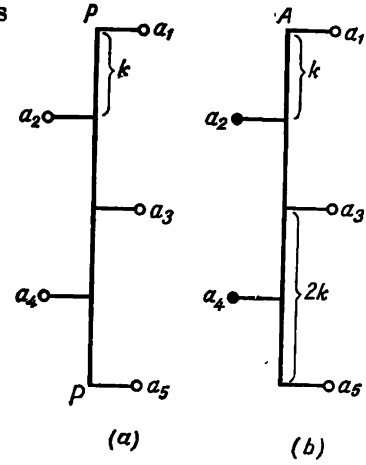


Fig. 215. A glide plane (*a*) and a twofold screw axis (*b*)

Sometimes a different designation is used: a curved arrow is placed over the L, showing the direction of rotation. Thus, $\overset{\frown}{L}^4$ means a right-handed fourfold screw axis, and $\overset{\frown}{L}^4$—a left-handed screw axis.

Operation of a onefold screw axis is equivalent to translation.

3. Translation Combined with Reflection, or Reflection Translation. The point a_1 (Fig. 215) will move to a_2 after translation over a distance k and reflection through the plane PP; repetitions of the operation will produce points a_3, a_4, a_5, etc. The plane PP is called a *glide plane*. It should not be confused with a twofold screw axis, as in the latter nodes (or groups of nodes) are rotated through 180°. The picture obtained is shown in Figs. 215 (*a*, *b*), in Fig. 215, *b* circles on one side are white, and on the other black.

SPECIFIC FEATURES OF SPACE LATTICE SYMMETRY

The symmetry of space lattices has the following specific features.

1. A line parallel to an axis of symmetry and passing through a lattice node becomes an axis of symmetry of the same degree for that lattice. A plane parallel to a plane of symmetry and passing through a node is a plane of symmetry for that lattice.

2. An axis of symmetry passing through a lattice node is a row of the lattice.

3. A plane passing through a lattice node in a direction perpendicular to an axis of symmetry of the lattice is a plane net.

4. A space lattice always has an infinite number of centres of symmetry. These centres are nodes, centres of parallelepipeds and faces, and midpoints of edges.

5. If a lattice has an n-fold symmetry axis (n being greater than 2), it also has n twofold axes perpendicular to the L^n axis.

TRANSLATION LATTICES

In 1855 A. Bravais derived all the possible patterns of space lattices which could be obtained by translation. He found that there could be 14 such lattices of four different types.

1. Primitive lattices, in which particles are located only at the apexes of parallelepipeds. Introduction of particles into various parts of the lattices produces more complex lattice types.

2. Base-centred lattices, where additional particles are located at the centre of bases or of any two parallel faces of a cell.

3. Body-centred lattices, in which there is a node in the centre of a parallelepiped, besides those at the apexes.

4. Face-centred lattices, in which the nodes are located at the apexes of parallelepipeds and in the middle of each face of a cell.

Translation lattices are distributed throughout the systems as follows (Table 11).

1. The triclinic system contains only one primitive lattice.

2-3. The monoclinic system has a primitive and a base-centred lattices.

4-7. The orthorhombic system has all the four types of lattices: primitive, base-centred, body-centred, and face-centred.

8. The trigonal (rhombohedral) system has only one primitive lattice with a rhombohedral cell.

9-10. The tetragonal system has a primitive lattice and a body-centred one.

11. The hexagonal system has only one base-centred lattice.

12-14. The cubic system has a primitive, a body-centred, and a face-centred lattices.

Table 11

Translation lattices

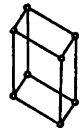
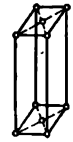
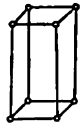
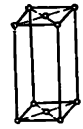
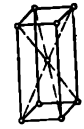
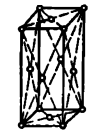
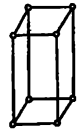
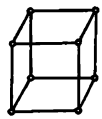
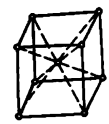
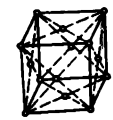
System	Primitive	Base-centred	Body-centred	Face-centred
Triclinic				
Monoclinic				
Orthorhombic				
Trigonal (rhombohedral)				
Tetragonal				

Table 11 (continued)

System	Primitive	Base-centred	Body-centred	Face-centred
Hexagonal				
Cubic				

Base-centred, body-centred, and face-centred lattices are easily obtained from primitive lattices by simple translation. For instance, a body-centred cubic lattice is obtained from a primitive lattice by a single translation, the extent and direction of which are determined by the components

$$\frac{a_I}{2}, \frac{a_{II}}{2}, \frac{a_{III}}{2},$$

where a is in this case the length of the cube edge in the direction of the axes *I*, *II*, *III*. A body-centred cubic lattice can be regarded as a combination of two primitive cubic lattices telescoped one into the other by the above method.

SPACE GROUPS

If translations differing in extent and direction are carried out, more complex lattices are obtained. In crystalline substances their character and number cannot be infinitely diverse, as they are limited to definite axes of symmetry (of the regular, inversion, and screw type). The regular combinations of points firstly developed by Fedorov and Schöenflies are called *space groups*, and there are 230 of them, distributed among the systems in the following numbers:

Triclinic system	—2
Monoclinic system	—13
Orthorhombic system	—59
Trigonal system	—25
Tetragonal system	—68
Hexagonal system	—27
Cubic system	—36
total	230

The regular arrangement of points can be visualized as a combination of several lattices telescoped one into another. In crystalline substances material particles occur in places of lattice nodes. As shown by X-ray studies these particles may be atoms, ions, molecules, complexes, or radicals. Each of the lattices constituting a space group has for its nodes particles of similar chemical composition and charge. The question naturally arises as to what types of bonds exist between particles in different cases.

TYPES OF BONDS BETWEEN MATERIAL PARTICLES IN REAL CRYSTALS

There are four principal types of bonds: ionic, or heteropolar, homopolar, or covalent, metallic, and residual.

1. Neutral atoms of some chemical elements easily lose their external (valency) electrons and thus become positively charged ions. Atoms of other elements are, on the other hand, short of a few electrons. Therefore, they easily pick up the electrons they lack and become negatively charged ions. Positive and negative ions are mutually attracted and produce crystal structures of the *ionic*, or *heteropolar* type.

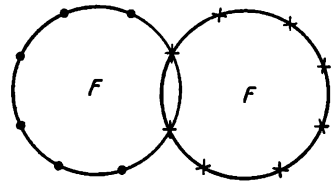


Fig. 216. Homopolar bonding of fluorine atoms

2. Stability of structures of the homopolar type is due to the presence of one or more electrons shared by two neighbouring atoms, i.e., electrons which constitute a part of both of the atoms simultaneously (Fig. 216).

3. Atoms of metals contain freely moving electrons. This explains the considerable heat and electrical conductivity of most metals. *Metallic bonding* is due to mutual attraction between positively charged atomic cores* and the aggregate cloud of electrons. Thus, valency electrons are common to all atoms.

* The core of an atom is an atom without outer electrons.

4. The nature of *residual bonding* is less clear than the other types. In this type of bonding the structural units are connected by the so-called *van der Waals forces* (gravitational forces as applied to elementary particles) or *residual* forces which are much weaker than the previous three types.

It is not always possible to draw distinct lines between the types of bonds. There are also bonds of an intermediate type. For instance, crystals of NiAs represent a compound whose properties can be explained partly by the ionic and partly by the metallic type of bonding. Different types of bonds between individual structural particles may exist in the same crystal at the same time.

CHAPTER XIII

X-ray Analysis of Crystal Structure

In 1895 Röntgen discovered an unusual type of radiation which he called X-rays. The nature of these rays remained obscure for a long time. In 1912 Laue found that these rays were of an electromagnetic nature. He succeeded in effecting their interference by using a zinc blende crystal (ZnS) as a three-dimensional diffraction grating. Laue's work made it possible to determine the wavelength of X-rays and to measure the spacing between material particles in crystal lattices. These spacings and wavelengths are measured in angstroms (Å$=10^{-8}$ cm).

X-rays are obtained in tubes from which air is almost completely evacuated. The rays emanate from an anode when it is bombarded by a high-velocity stream of electrons. The tube voltage runs into thousands and tens of thousands of volts. Direct current used is of the order of a few milliamperes. X-ray waves, similarly to those of visible light, differ in length—from 0.1 to 10.0 Å.

Short-wave radiation is called *hard* radiation, long-wave radiation is *soft*. The character of radiation, including its intensity and wavelength, depends on the chemical composition of the anode metal and on the voltage of the tube circuit. The rays emanate at a small angle from the surface of the usually flat anode. If the waves are all of one definite length, the radiation is called *monochromatic*. If it contains waves of different length, the radiation is called *white* or *polychromatic*, by analogy with visible light.

To obtain monochromatic radiation, a voltage is selected depending on the metal of the anode, and a filter is placed in the path of the rays to suppress all radiation except that of a definite wavelength. The filters are chosen in accordance with the wavelength of the characteristic radiation. A manganese filter is used with an iron anode, a nickel filter with a copper anode, a zirconium filter with a molybdenum anode. Instead of the pure metals, their oxides or salts can be used for filters. They are introduced into a celluloid film in the amount of 0.0042 g of manganese, 0.0067 g of nickel, or 0.02 g

of zirconium per 1 sq centimetre of film. Monochromatic rays used for the analysis of crystal structure are usually of considerable wavelength: $\lambda=1.539$ Å for a copper anode, and $\lambda=1.934$ Å for an iron anode.

As we see it, the interference of X-rays is caused by the crystal lattice in the following manner. The rays from the anode of a tube, or *primary* rays, impinge on a crystal, whose material particles begin to vibrate and emit rays of the same wavelength but of much lower intensity. These rays are called *secondary*, and as they have a very low intensity their presence can be detected only if they are enhanced by interference. G. V. Wulff, W. H. Bragg and W. L. Bragg drew up a diagram and worked out a formula for this phenomenon.

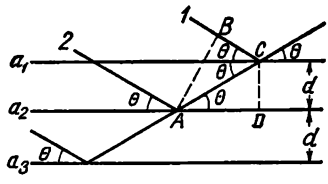


Fig. 217. A drawing to the derivation of the Bragg-Wulff equation

Let us imagine a section through a crystal lattice (Fig. 217). Plane nets a_1, a_2, a_3, etc. are normal to the plane of the drawing. Material particles of the crystal are located in the nodes of the nets. A bundle of parallel X-rays (primary rays) strikes this series of planes at an angle θ. The angle is made by the direction of the rays and the plane of incidence (and not the normal to this plane, as in optics). The θ angle is therefore called a *glancing angle*.

The secondary rays emitted by atoms in the planes a_1, a_2, a_3, etc. interfere, as there is a phase difference, Δ, between them. The interference leads to an increase in intensity, if the phase difference represents a whole number of waves, i. e., if $\Delta=n\lambda$, where $n=1, 2, 3$, etc. The phase difference depends on the glancing angle θ and on d, the spacing between the plane nets a_1, a_2, a_3, etc. The three values are related to each other in the following way. The phase difference of rays *1* and *2* is $\Delta=AC-BC$. From the right triangle ABC we have:

$$BC = AC\cos 2\theta,$$

hence,

$$\Delta = AC(1-\cos 2\theta) = 2AC\sin^2\theta.$$

From the triangle ADC in which $CD=d$, i. e., interplanar spacing, we have:

$$AC = \frac{CD}{\sin\theta} = \frac{d}{\sin\theta},$$

hence,

$$\Delta = n\lambda = 2\frac{d}{\sin\theta}\cdot\sin^2\theta = 2d\sin\theta.$$

This is the Bragg-Wulff formula, the principal formula of X-ray analysis of crystal structure.

The glancing angle θ can be determined experimentally. Knowing the angle and the wavelength λ we can determine the interplanar spacing d. If d is known, λ can be calculated. In determining θ, λ, and d monochromatic radiation of constant wavelength is used.

There are four principal methods of crystal-structure analysis.

1. Laue Method. A bundle of X-rays of different wavelengths impinges at 90° on the plane of a crystal plate 0.2-1.0 mm thick or on a small crystal. On their way through the crystal the rays encounter plane nets with different spacings d. The nets make various angles θ with the direction of the rays. Some combinations of d, θ and λ satisfy the conditions of the Wulff-Bragg formula with the resulting increase in radiation intensity.

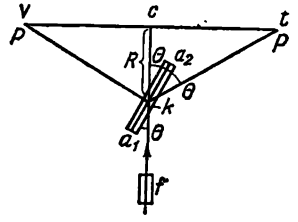


Fig. 218. Laue method

The Laue method is shown in Fig. 218. Primary rays pass through the crystal k via the inlet diaphragm f and produce a central black spot at the point C on the photographic plate PP. We recall that the bundle consists of rays of different wavelength. The number of plane nets forming various angles θ with the direction of the incident ray is infinitely large. Under these conditions some planes will increase the intensity because of the interference of secondary rays, which show up on the photographic plate as less pronounced spots surrounding the central spot.

In our example (see Fig. 218) a_1a_2 is one of the possible plane nets, therefore, θ is the corresponding glancing angle, t is the spot on the photographic plate, V is the gnomonic projection of the a_1a_2 plane or of the crystal face corresponding to it.

In a photograph made by this method we can measure the distance from the centre C to any spot t. The value of R, the distance from the crystal to the photographic plate, can also be measured. Then, insofar as $Ct=R \tan 2\theta$, we can determine the θ angle for the corresponding plane, and plot the spot t on a gnomonic or stereographic projection.

Thus, the Laue method enables us to investigate the symmetry of the crystal lattice and to determine the orientation of plates which were cut from a crystal at unknown angles to the elements of symmetry of the crystal.

2. Bragg Method. A bundle of monochromatic X-rays impinge on the crystal k via the diaphragm S (Fig. 219). The crystal is mounted on a stage rotating about a vertical axis (i.e., perpendicular to the plane of the drawing). Secondary rays intensified by interference are

registered not photographically but with the aid of an ionization chamber v. The chamber is a hollow lead cylinder filled with a gas, e.g., SO_2. The gas may be ionized by X-rays. Two electrodes, l and t, are connected to a storage battery B. An electrometer E showing the degree of ionization is connected in the same circuit. Ionization takes place when the angle θ corresponds to the interplanar spacing d of that crystal face on which the primary bundle impinges. To find the value of the angle θ the ionization chamber is rotated about the axis

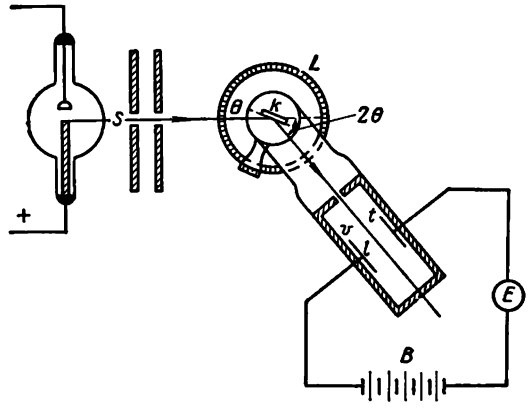


Fig. 219. Bragg method

of rotation of the stage with the crystal. Readings are taken off the dial L. Ionization (differing in intensity) may take place at different values of the angle θ. Experience has shown that the ratio of the sines of these angles is as 1 : 2 : 3, etc. For instance:

$$\theta_1 = 10°40', \quad \sin\theta_1 = 0.185 = 1 \times 0.185 = 1 \sin\theta_1$$
$$\theta_2 = 21°40', \quad \sin\theta_2 = 0.370 = 2 \times 0.185 = 2 \sin\theta_1$$
$$\theta_3 = 33°40', \quad \sin\theta_3 = 0.555 = 3 \times 0.185 = 3 \sin\theta_1$$

Reflection* occurring at the minimum value of θ is called *reflection of the first order*; that at the next larger angle—*reflection of the second order*, etc. The values 1, 2, 3, etc. correspond to the values of n in the equation

$$n\lambda = 2d \sin\theta.$$

W. H. Bragg and W. L. Bragg built an instrument—an X-ray spectrometer—in accordance with the scheme outlined. Their work

* This word is used hereinafter for brevity. Actually there is no reflection, as can be seen from the foregoing.

with this instrument resulted in the above formula and in many remarkable investigations of crystal structure.

3. Debye-Scherrer Method, or Powder Method. It has been said that in photographing by the Laue method polychromatic rays and a single crystal are used, because in the case of monochromatic rays there is very little chance of rays of a definite wavelength striking a plane net with a corresponding interplanar spacing at an angle θ required by the Bragg-Wulff formula, so that the reflected beam would be within the boundaries of the photographic plate.

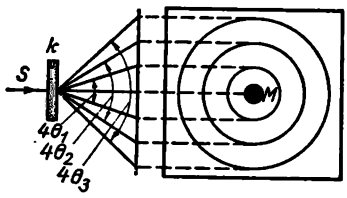


Fig. 220. Debye-Scherrer method: *S*—bundle of rays; *k*—crystal; *M*—central spot

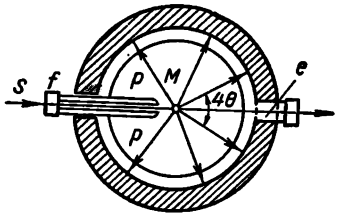


Fig. 221. Photographing by the Debye method

Instead of a single crystal Debye and Scherrer began using powdered crystals, i.e., a multitude of minute crystals, and monochromatic rays. Compressed into a rod sample, the tiny crystals have different orientations, and therefore the possibility of interference which depends on the ratio of λ, d, and θ greatly increases. As a result, instead of individual spots whole series of spots are obtained (Fig. 220) which, merging, produce curves on a photographic plate or film.

The chamber is cylindrical in shape (Fig.221), and the photographic film *PP* is bent along its inner surface.Primary rays enter the chamber through the diaphragm *f*, strike the sample *M* which is set up perpendicularly to the plane of the drawing, and leave through the aperture *e*. Secondary rays interfere diverging from the sample. The rays that intensify each other produce a number of cones intersecting the cylindrically bent photographic film *PP*. At the intersection of the cones and the film, curves are obtained which are called *arcs* or simply *lines*. Figs. 220 and 221 show that the angles between the arcs of the same cone are 4θ.

On a stretched film the arcs appear as shown in Fig. 222. If the distances between symmetrical lines are designated as l_1, l_2, l_3, etc. and the diameter of the cylindrical film as D, the relation

$$\frac{1}{\pi D} = \frac{4\theta}{360^\circ}$$

will show that

$$\theta = \frac{90^\circ}{\pi D} l$$

or

$$\theta = kl,$$

where $k = \frac{90^\circ}{\pi D}$ is a constant factor for a particular chamber.

How many lines can there be in a photograph, and what does their number depend upon? Theoretically the number can be very great, as it depends on an infinitely large number of values of d, but actually it is relatively small for the following reasons.

The values of d are repeated in symmetrical lattices. For instance, in a primitive cubic lattice d is the same in all the three mutually perpendicular directions. Crystals oriented in the rod at a corresponding angle θ with respect to the primary beam will give similar beam

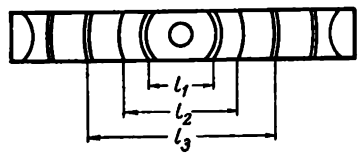


Fig. 222. Debye-Scherrer powder photograph

cones in three positions, therefore the intensity of the arcs will be at its greatest. There are two such positions for tetragonal lattices. In orthorhombic lattices all the three principal interplanar spacings are different and the crystals give a greater number of lines, but of lower intensity. The same is true of the monoclinic and triclinic lattices. Hence, a small number of high-intensity lines denotes a cubic lattice. In the intermediate systems the number of lines increases and their intensity decreases. The lower systems are characterized by a very large number of low-intensity lines.

The Debye-Scherrer method has the advantage of not requiring large single crystals, and almost any substance can be ground into powder. The study and measurement of the distances between the lines and of the line intensities help to solve many important problems, for instance:

(a) a crystalline substance can be distinguished from an amorphous one: the former produces lines on a photograph, the latter does not;

(b) if photographs are made before and after treatment (by heat, mechanically, or otherwise) of a crystalline substance, their comparison will reveal any alterations in the lattice;

(c) with the aid of standard photographs of known chemical compounds their presence may be detected in an unknown mixture;

(d) a substance, e.g., a mineral, can be determined if its powder photograph is compared with the standard photographs in a mineralogical determinative manual;

(e) the size of the unit cell and the type of the lattice can be determined in simple cases.

4. **Rotation method** is a combination of the Laue and Debye-Scherrer methods. The use of a single crystal identifies this method with the former, except that the crystal is definitely oriented; the use of monochromatic rays identifies it with the latter, thus making it possible to use the Wulff-Bragg formula in interpreting photographs, since the wavelength λ is known.

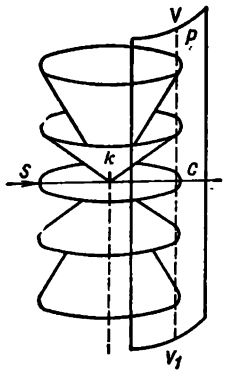


Fig. 223. Rotation method

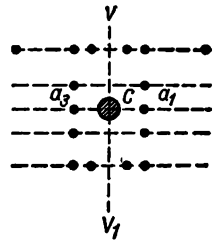


Fig. 224. X-ray photograph of rotation

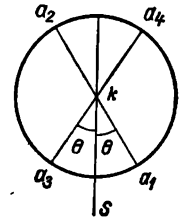


Fig. 225. Rotation method

This method requires a small crystal, preferably somewhat elongated, of 0.2-0.05 mm in cross-section. During exposure the crystal is rotated at a speed of 10-15 revolutions per hour. The axis of rotation should coincide with an edge of the crystal, i.e., with a row of the lattice.

Plane nets of a crystal may be positioned at various glancing angles θ to the primary rays. At some values of θ interference occurs, intensifying the reflected rays, which produce a series of cone surfaces (Fig. 223). The latter, crossing a cylindrical photographic film P, produce a number of horizontal lines (Fig. 224) which are called *layer lines*.

Each net gives two spots which are symmetrical with respect to the central vertical plane VV_1 (see Figs. 224 and 225, a_3 and a_1), because during a complete revolution of the crystal k the net twice occupies a position at the same angle θ to the incident rays S (Fig. 225).

Since in this case it is a single crystal that is photographed, and not powder as in the Debye-Scherrer method, the cone surfaces are inter-

mittent and not continuous, and reflections are recorded on the film only at definite points. The location of these points corresponds to the plane net position required for an increase in intensity caused by interference at a definite value of the angle θ.

Nets which are parallel to the rotation axis give spots on the so-called *zero line* which passes through the central spot of the photograph. Nets which are inclined to the axis of rotation give lines located symmetrically above and below the zero line. Nets which are perpendicular to the axis of rotation give no reflections.

The VV_1 plane which is parallel to the axis of rotation and passes through the central spot C is called the principal plane (see Figs. 223 and 224).

If the direction of the axis of rotation is parallel to the dense row of the lattice and therefore the layer lines are perpendicular to it, the parameter J of this row, i.e., its interplanar spacing, is determined from the formula:

$$J = \frac{n\lambda}{\sin \mu_n},$$

where n = number of the layer line (counting from the zero line)
μ_n = angle obtained from the equation

$$\tan \mu_n = \frac{e_n}{R},$$

where e_n = distance to the nth layer line from the zero line
R = radius of the cylindrical film.

If three photographs can be taken, the rotation method enables the size of the crystal cell to be easily determined. The crystal should be so oriented that in each case the axis of rotation is parallel to one of the three principal edges of the elementary parallelepiped.

CHAPTER XIV

Fundamentals of Crystal Analysis. Concepts of Crystal Chemistry

We shall here examine some of the most elementary methods of determining the structure of crystalline substances, using metallic copper as an example. How are we to determine the type of its lattice? Since copper crystallizes in the cubic system, its lattice may be one of three types: primitive, face-centred, or body-centred. Let us analyse the relationship of the three interplanar spacings, d_{100}, d_{110}, and d_{111} in these cases.

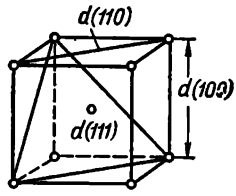


Fig. 226. Primitive cubic unit cell

In a primitive lattice (Fig. 226) d_{100} is equal in length to a cube edge which we shall designate a; d_{110} is equal to half the diagonal of a square of the side a, in other words,

$$d_{110} = \frac{a\sqrt{2}}{2}.$$

The interplanar spacing normal to an octahedral face is equal to one-third of the spatial diagonal of a cube, i. e.,

$$d_{111} = \frac{a\sqrt{3}}{3}.$$

Hence,

$$d_{100} : d_{110} : d_{111} = a : \frac{a\sqrt{2}}{2} : \frac{a\sqrt{3}}{3} = 1 : 0.71 : 0.58.$$

For a face-centred lattice:

$$d_{100}:d_{110}:d_{111}=\frac{a}{2}:\frac{a\sqrt{2}}{4}:\frac{a\sqrt{3}}{3}=1:0.71:1.15.$$

Finally, for a body-centred cubic lattice we have:

$$d_{100}:d_{110}:d_{111}=\frac{a}{2}:\frac{a\sqrt{2}}{2}:\frac{a\sqrt{3}}{6}=1:1.41:0.58.$$

An X-ray photograph of a metallic copper crystal gives the following interplanar spacing values:

$$d_{100}:d_{110}:d_{111}=1.80\text{Å}:1.28\text{Å}:2.07\text{Å}.$$

The ratios obtained for copper indicate a face-centred lattice with a cube edge $a=3.60$ Å. We can check this result by finding the number of copper atoms per structural cell using the equation

$$n=\frac{V\rho}{1.66\times10^{-24}M},$$

where n = number of atoms
V = cell volume
ρ = specific gravity of copper
M = molecular (atomic) weight of copper
1.66×10^{-24} = weight of a hydrogen atom in grams.

In the case under consideration

$$n=\frac{(3.60)^3\times10^{-24}\times8.86}{1.66\times10^{-24}\times63.6}=3.96.$$

As n must be a whole number, we make it 4; the difference of 0.04 may be due to experimental errors in the determination of a, ρ, and M.

The primitive lattice contains one atom per cell. This can be proved as follows.

1. In the primitive lattice material particles are located only at the apexes of the cell angles.

2. One apex is common to eight parallelepipeds of a crystal lattice, consequently resulting in one-eighth of an atom per cell apex.

3. Since the cell has eight apexes, it must therefore contain one atom.

The same considerations will lead us to conclude that a body-centred lattice has two atoms per cell, and a face-centred lattice has four. The latter agrees with the result obtained in our investigation of copper.

Lattices composed of material particles usually fall in several definite types, on the basis of the following features.

1. The state of material particles forming the lattice. Lattices may be *molecular*, *ionic*, *atomic*, *complex-ionic*, etc.

2. The number of elements in the formula. Lattices may be of the AX, AX_2, A_2X_3, and other types.

3. The nature of particle arrangement. The type of the lattice gets its name from some characteristic compound with a similar structure, e.g., the type of rock salt, caesium chloride, diamond, graphite, etc. The number of such types is great.

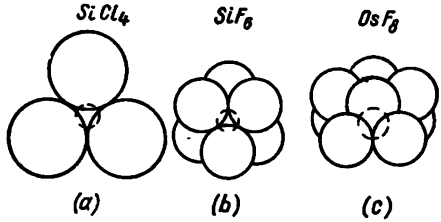


Fig. 227. Arrangement of ions at coordination numbers 4, 6, and 8

To give a better idea of the structure and to facilitate the determination of the space occupied by particles the term *coordination number* has been introduced. This term denotes the number of atoms adjacent to a given atom and located at equal distances from it. Fig. 227 shows the arrangement of the ions at different coordination numbers: 4 for $SiCl_4$, 6 for SiF_6, and 8 for OsF_8.

The size of particles, i.e., *ionic and atomic radii*, are of the utmost importance for the determination of the arrangement of the particles in a crystal lattice.

Ionic and atomic radii were determined in 1926 by V. M. Goldschmidt. Those which are especially important for mineral structures are listed in Table 12.

Table 12

I	II	III	IV	V	VI	VII	VIII
Na^{1+} 0.98	Mg^{2+} 0.78	Al^{3+} 0.57	C 0.77	N 0.71	O^{2-} 1.32	F^{1-} 0.83	Fe^{2+} 0.83
K^{1+} 1.33	Ca^{2+} 1.06		Si^{4-} 1.98	As^{3+} 0.69	S^{2-} 1.74	Cl^{1-} 1.81	Co^{2+} 0.82
Cu^{+} 1.27	Zn^{2+} 0.83		Si^{4+} 0.39	Sb^{3+} 0.90	S^{6+} 0.34	Mn^{2+} 0.91	Fe^{3+} 0.67
Cs^{1+} 1.65	Sr^{2+} 1.27		Ti^{4+} 0.64		Cr^{3+} 0.65	Br^{1-} 1.96	Ni^{2+} 0.78
	Ba^{2+} 1.43		Zr^{4+} 0.87		Mo^{4+} 0.68	I^{1-} 2.20	
			Sn^{4+} 2.15		W^{4+} 0.68		
			Sn^{4+} 0.74		U^{4+} 1.05		

If the particles are considered as incompressible spheres, the structure should be stable when positively charged cations are surrounded with negatively charged anions so that they are all in close contact

with each other. Such an arrangement is possible for cations and anions of definite size at a definite coordination number.

In the case of the coordination number 6, one cation, a sphere of a radius r_k (Figs. 227, *b* and 228) is surrounded by six anions—spheres of a radius r_a located in space as the apexes of an octahedron.

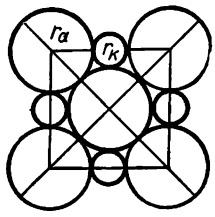


Fig. 228. A cross-section through the centres of cations and anions

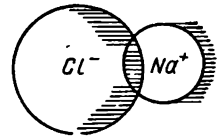


Fig. 229. Polarization of ions

From a cross-section (see Fig. 228) taken through the centres of four anions it may be seen that the side of the square is equal to $2r_a+2r_k$, hence its diagonal $2r_a+2r_a$ is

$$(2r_k+2r_a)\sqrt{2}=4r_a.$$

Multiplying both sides of the equation by $\sqrt{2}$ we obtain

$$4r_k+4r_a=4r_a\sqrt{2}.$$

Dividing the equation by $4r_a$ we obtain

$$\frac{4r_k}{4r_a}+\frac{4r_a}{4r_a}=\frac{4r_a\sqrt{2}}{4r_a}$$

or, cancelling,

$$\frac{r_k}{r_a}=\sqrt{2}-1;\quad r_k:r_a=\sqrt{2}-1=0.41.$$

When the radius of an anion is smaller than that of a cation, we obtain the reverse ratio, i. e.,

$$\frac{1}{0.41}=2.41.$$

The values obtained, 0.41 and 2.41, respectively, are the two limits of stability (the lower and the upper limits) of structures with the coordination number 6.

For other coordination numbers we have the following limits of stability (Table 13).

Table 13

Coordination number	Pattern	Limits of stability
2	Dumbbell	From 0 to 0.15 and from 6.45 to ∞
3	Triangle	From 0.15 to 0.22 and from 4.45 to 6.45
4	Tetrahedron	From 0.22 to 0.41 and from 2.41 to 4.45
6	Octahedron	From 0.41 to 0.73 and from 1.37 to 2.41
8	Cube	From 0.73 to 1.37
12	Cubic octahedron	1

The values of ionic radii are not constant, however, because ions are not truly incompressible spheres. An ion within an electric field is distorted under the influence of surrounding ions of opposite charge; this is known as *ion polarization* (Fig. 229). The greater the radius of the ion and the lower its charge, the greater the degree of polarization. This is mainly the property of anions. Cations in most cases are smaller in size and with a higher charge. They do not polarize so strongly, but are capable of causing polarization of adjacent anions.

The principal law of crystal chemistry has been stated by V. M. Goldschmidt as follows: the *structure of a crystal is determined by the number of its structural units, by the ratio of their size, and by their polarization properties.*

The relationship between the chemical composition of various substances and their crystal form is expressed by the following approximate law by P. Groth: *the simpler the chemical composition of a substance, the more complicated in most cases its symmetry.*

Groth's law, although approximate, is still true in a great number of cases. Thus, elements which are very simple chemically crystallize most frequently in the cubic or hexagonal system, as can be seen from the following.

27 elements crystallize in the cubic system, 8 in the hexagonal system and 13 in both at the same time. The latter is possible because of a special property of substances known as *polymorphism.* This property, inherent both in elements and in various compounds, consists in the ability of crystallizing in several solid phases with differing constants of their crystal lattices. Depending on the physicochemical conditions of formation, substances produce crystals differing in external form and physical properties. Each such phase is called a *modification* of the given substance.

Polymorphism is a frequently occurring phenomenon of crystal formation occurring, e.g., in diamond (cubic system) and graphite (hexagonal system), sulphur which has several modifications (orthor-

hombic, monoclinic, hexagonal), zinc sulphide, ZnS, which crystallizes in the cubic (sphalerite) and hexagonal (wurtzite) systems.

Titanium dioxide, TiO_2, has three modifications: rutile (tetragonal system), anatase (also tetragonal system but of a different structure), and brookite (orthorhombic system). Ammonium nitrate, NH_4NO_3, has several modifications which grade one into another with changes in temperature. A very characteristic example is that of the minerals calcite and aragonite which have the same composition, $CaCO_3$, but differ radically in habit and physical properties of their crystals. Calcite crystallizes in the $L_6^3 3L^2 3PC$ class (trigonal system), and aragonite (orthorhombic system) in the $3L^2 3PC$ class.

We shall here mention another phenomenon which is very important to the study of natural crystals (minerals). This is *isomorphism*, which was discovered in 1819 by Mitcherlich. *Substances with analogous chemical composition and with unit cells of closely similar crystallographic constants are said to be isomorphous.*

Chemical formulae are regarded as analogous if the numbers of positive and negative ions of one substance are equivalent to the corresponding numbers of the other, e.g., $BaSO_4$—KBF_4, $CaTiO_3$—$KMgF_3$.

Isomorphism is *perfect* if two substances will give mixed crystals (i.e., of variable composition) at any quantitative ratios of these substances.

Isomorphism is *imperfect* when two substances will produce mixed crystals only at *definite* ratios of the two.

To illustrate the point let us look at the following series of carbonate salts of alkaline-earth metals:

(1) magnesite (magnesial spar $MgCO_3$) with the $a : c$ ratio$=0.8112$;
(2) calcite (lime spar $CaCO_3$) with $a : c=0.8543$;
(3) smithsonite (zinc spar $ZnCO_3$) with $a : c=0.8063$;
(4) otawite (cadmium spar $CdCO_3$) with $a : c=0.8090$;
(5) rhodochrosite (manganese spar $MnCO_3$) with $a : c=0.8184$, and
(6) siderite (iron spar $FeCO_3$) with $a : c=0.8184$.

They all crystallize in the scalenohedral class ($L_6^3 3L^2 3PC$) of the trigonal system and have perfect rhombohedral cleavage parallel to $(10\bar{1}1)$. Magnesite and siderite give a continuous isomorphous series $(Fe, Mg)CO_3$ and are examples of perfect isomorphism. Calcite and magnesite, on the other hand, yield only one substance of intermediate composition—dolomite, $MgCa(CO_3)_2$, and are examples of imperfect isomorphism.

Another example of perfect isomorphism is the extensive series of feldspars which are mixtures of albite, $NaAlSi_3O_8$, anorthite, $CaAl_2Si_2O_8$.

Besides isomorphism there is also *isogonism*. For instance, Chile nitre, $NaNO_3$, crystallizes in the same rhombohedra as calcite,

$CaCO_3$; the angles of these rhombohedra are identical, but the substances produce no mixed crystals.

Isomorphism may also be *isovalent* and *heterovalent*. In the first case the valencies must be equal. For instance, in isomorphous mixtures of KH_2PO_4 and KH_2AsO_4 both phosphorus and arsenic are pentavalent. In the case of heterovalent isomorphism the ions replacing each other have different valencies, e.g., $FeCO_3$ and $ScBO_3$, where the divalent iron is replaced by trivalent scandium, and the tetravalent carbon by trivalent boron. Thus, it is sufficient for ions to be of more or less similar dimensions to replace each other.

TYPICAL STRUCTURES

Elements. 1. Copper, as has already been mentioned, has a cubic face-centred lattice (Fig. 230). The cube edge $a=3.60$ Å. Of similar structure are gold ($a=4.07$ Å), silver ($a=4.08$ Å), γ-iron ($a=3.63$ Å), and many other elements.

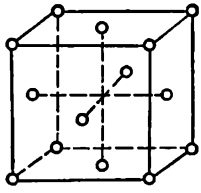


Fig. 230. Structure of copper

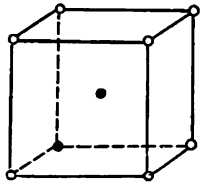


Fig. 231. Body-centred lattice

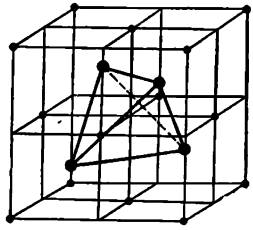


Fig. 232. Structure of diamond

2. α-, β-, and δ-iron have a body-centred cubic lattice (Fig. 231) with edges measuring 2.80, 2.90, and 2.93 Å, respectively. The same structure is characteristic of metallic sodium and potassium; for the former $a=4.30$ Å, for the latter $a=5.20$ Å.

3. If a cubic face-centred cell is cut by three mutually perpendicular planes into eight small cubes and if additional single atoms are placed in the centres of the two upper cubes (front right-handed cube and rear left-handed cube) and the two lower cubes (front left-handed cube and rear right-handed cube), the structure of the diamond is obtained: $a=3.55$ Å (Fig. 232). This structure can also be visualized as consisting of atoms in a tetrahedral surrounding (Fig. 233).

4. Graphite has a layered hexagonal lattice (Fig. 234). The side of each hexagon base $a=2.46$ Å, the height of the cell $c=6.82$ Å, the spacing between layers $c/2=3.41$ Å.

5. Metallic magnesium, as well as zinc, cadmium, titanium, and some other elements, has a hexagonal base-centred cell with three

more atoms in the middle positioned in the centres of the three of the six trigonal prisms into which the cell can be broken by three vertical planes (Fig. 235). For magnesium the side of the base $a=3.20$ Å, the height $c=5.20$ Å.

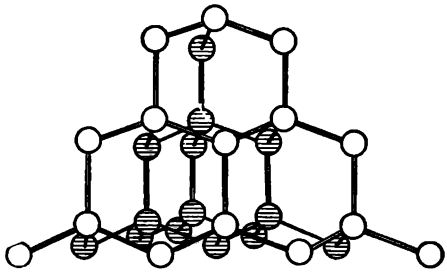


Fig. 233. Structure of diamond consisting of atoms in tetrahedral surroundings

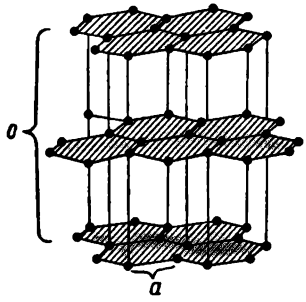


Fig. 234. Structure of graphite

AX* Compounds. 1. *Sodium chloride* (NaCl) *type*. The structure is based on a face-centred cubic lattice. Sodium and chlorine alternate at the apexes of small cubes (Fig. 236). The coordination number is 6. Numerous other binary compounds have a similar structure.

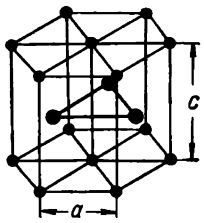


Fig. 235. Structure of zinc

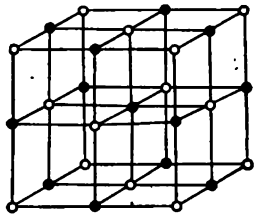


Fig. 236. Structure of sodium chloride

2. *Caesium chloride* (CsCl) *type*. The structure is based on a body-centred cubic lattice with the cube edge $a=4.11$ Å (Fig. 237, *a*). Ions of one element are at the apexes of the cube, while ions of the other are at the centres. The structure may be visualized as two primitive cubic lattices telescoped one into the other with translations $^1/_2$, $^1/_2$, $^1/_2$ (Fig. 237, *b*).

* The first letters of the alphabet, *A*, *B*, *C*, denote cations, the last, *X*, *Y*, *Z*—anions. *U*, *V*, *W* denote radicals which form complex anions.

3. *Zinc blende* (ZnS) *type*. The structure of ZnS is like that of the diamond, a face-centred cube broken into eight small cubes (Fig. 238). Atoms of sulphur are located at the apexes and centres of the faces of the large cube. Atoms of zinc are located in the four smaller cubes. They are staggered at the centres of the two upper and the two lower cubelets. These centres form a regular tetrahedron.

4. *Boron nitride* (BN) *type* (Fig. 239) is very close to the graphite type. The layers consist of atoms located at the apexes of regular hexagons. Each atom of an element is surrounded by three atoms of the other.

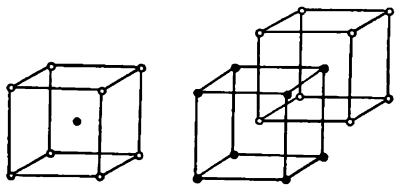


Fig. 237. Structure of caesium chloride

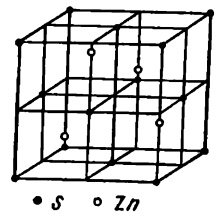


Fig. 238. Structure of zinc blende

AX_2 and A_2X Compounds. In the structures of these compounds two coordination numbers can be determined: of A with respect to X, and of X with respect to A.

1. *Rutile* (TiO_2) *type*. Coordination numbers 6 and 3 (Fig. 240); a=4.52 Å, c=2.91 Å.

2. *Cuprite* (Cu_2O) *type*. Coordination numbers 4 and 2 (Fig. 241); a=4.26 Å.

3. *Fluorite* (CaF_2) *type*. A face-centred cube of calcium ions is divided into eight cubelets. The centres of the cubelets are occupied by fluorine ions (Fig. 242); a=5.45 Å. The same structure can also be represented as in Fig. 243.

4. *Cadmium iodide* (CdI_2) *type* (Fig. 244). Coordination numbers 5 and 3. CdI_2 is an example of layered structure. The layers of cadmium atoms lie between two layers of iodine atoms. The three-layered groups of atoms alternate in the structure. The bonds within the triple layers are much stronger than between these groups. This is the reason for cleavage occurring parallel to the layers.

Silicates. The structure of these compounds, which are often chemically complex, is controlled primarily by the ratio of the number of silicon atoms to that of oxygen atoms. If the silicon-oxygen ratio is 1 : 4, the silicon ion is surrounded by four oxygen ions and *tetrahedral structures* develop (Fig. 245). At a 2 : 7 ratio one oxygen ion is shared by two adjacent tetrahedra (Fig. 246). At a 1 : 3 ratio *rings*

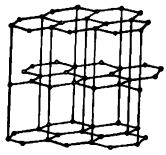


Fig. 239. Structure of boron nitride

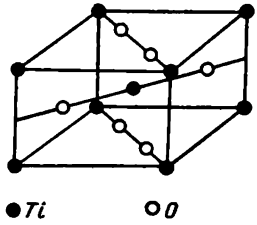


Fig. 240. Structure of rutile

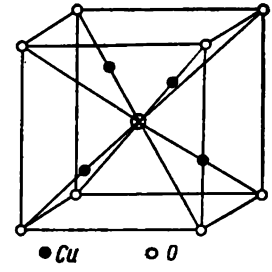


Fig. 241. Structure of cuprite

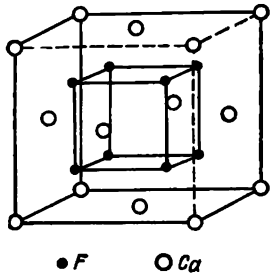


Fig. 242. Structure of fluorite in the form of a cube

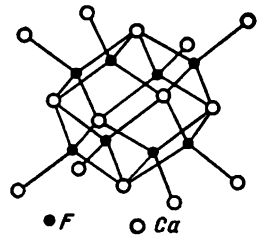


Fig. 243. Structure of fluorite in the form of a rhombic dodecahedron

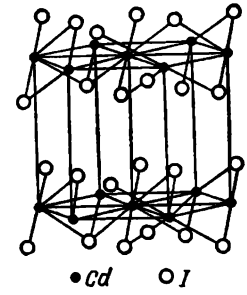


Fig. 244. Structure of cadmium iodide

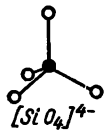


Fig. 245. Structure of silicates with SiO_4

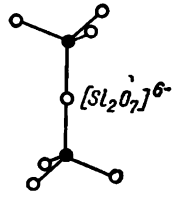


Fig. 246. Structure of silicates with Si_2O_7

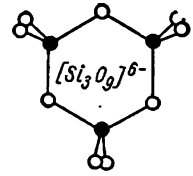


Fig. 247. Structure of silicates with Si_3O_9

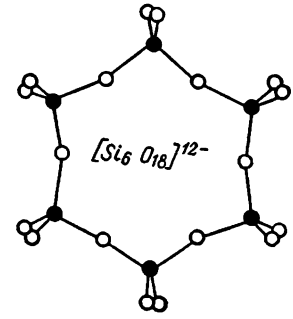


Fig. 248. Ringed structure of silicates

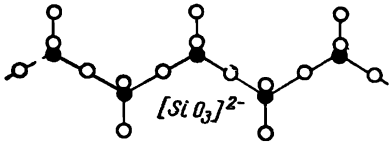


Fig. 249. Chain structure of silicates

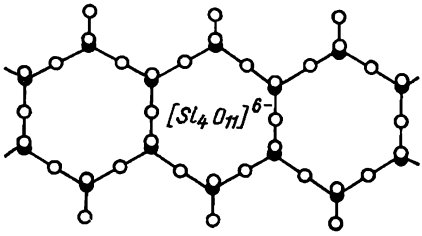


Fig. 250. Tape structure of silicates

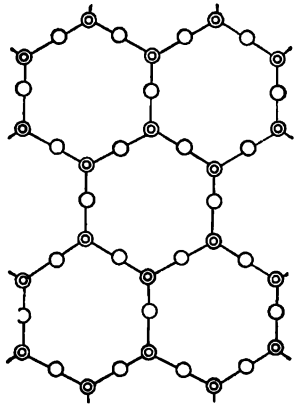


Fig. 251. Sheet structure of silicates

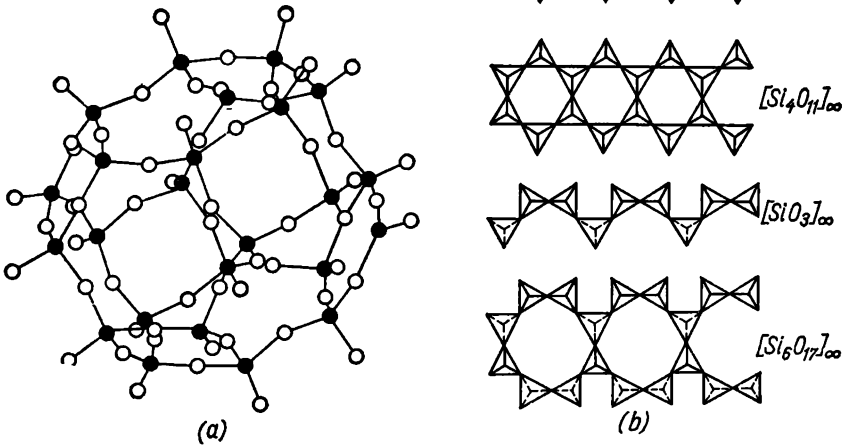


Fig. 252. Framework structure of silicates

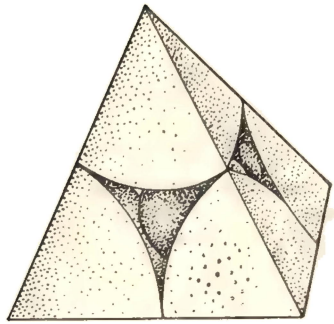


Fig. 253. Centres of spheres form a tetrahedron

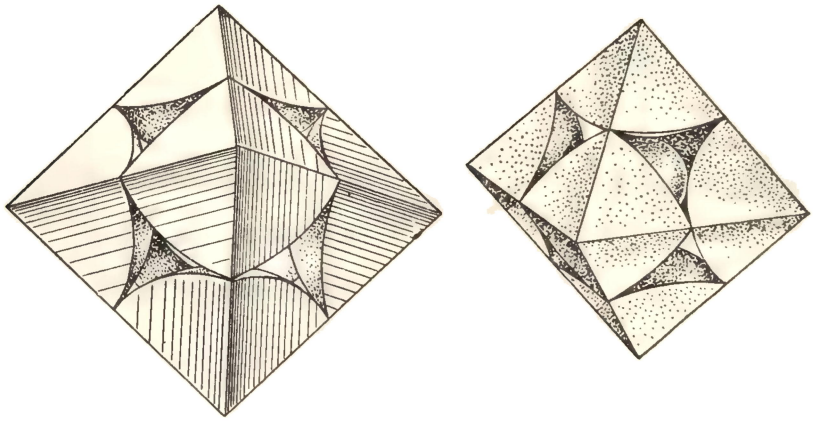


Fig. 254. Centres of spheres form an octahedron

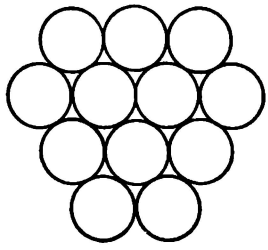


Fig. 255. Filling a plane with spheres (single layer)

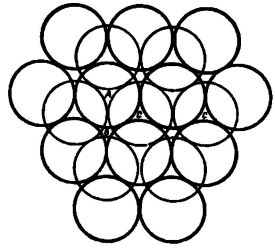


Fig. 256. Filling a plane with spheres (two layers)

are formed (Figs. 247 and 248). If the ratio is expressed by the formula Si_nO_{3n}, a chain structure results (Fig. 249).

Further complexity in the formula results in *tape* (Fig. 250), *sheet* (Fig. 251) and *framework* (Fig. 252) structures.

CLOSE-PACKED STRUCTURES

It has been suggested by Pauling that we should think of structures as consisting of polyhedra and not of spheres. The change from spherical packing to tetrahedra and octahedra is shown in Figs. 253 and 254. The centres of anions surrounding a cation are connected by lines. When the coordination number is 4, tetrahedra are obtained (Fig. 253), while octahedra we obtain when it is 6 (Fig. 254).

N. Belov has evolved polyhedra corresponding to other coordination numbers. His work is based on the principle of *close-packed structures*. This principle can be explained as follows.

Let us take spheres of uniform size and arrange them in a layer on a plane so that they touch each other (Fig. 255). When a second layer is built on top of the first one (Fig 256), the spheres of the former will fit into the depressions in the latter. The first and the second layers can be arranged only in one way, provided that they have similar diameters and touch each other. The third layer, however, can be arranged in two ways. However, not all the depressions between the spheres of the second layer are similar. Under some depressions (marked *A* and *C* in Fig. 256) there are spheres of the first layer, and under others (marked *B*) there are none. It follows that by placing the spheres of the third layer we can obtain two different types of close-packed structure.

If the spheres of the third layer are placed in depressions *B* under which there are no spheres of the first layer (Fig. 256), we shall have a close-packed *cubic* structure. If we place the spheres of the third layer so that they are just above the spheres of the first layer (i.e., in depressions *A*), we shall have a close-packed *hexagonal* structure. In the latter case there will be vertical gaps in the structure into which thin rods could be inserted that would pass through the entire structure. In both cases the spheres will occupy 74.05 per cent of the total volume of the structure.

CHAPTER XV

Optical Properties of Crystals

Optical constants are the most important physical properties of crystals for geological prospectors. The methods of determining the mineralogical composition of rocks by inspection of thin sections under the microscope are based on optical properties.

In this course it is possible to give only the most elementary data on the optical properties of crystals and on the methods of microscopic examination. More detailed descriptions may be found in books on petrography.

Several theories have been suggested to explain the nature of the phenomenon of light. The discussion below is based on the mechanical theory of Huygens, slightly modified in accordance with the more recent one of Maxwell.

PRINCIPLES OF GEOMETRICAL OPTICS

Light is regarded as a phenomenon caused by harmonic vibration of electric and magnetic vectors perpendicular to its direction of propagation. The character of harmonic vibration of the electric and magnetic vectors is shown in Fig. 257.

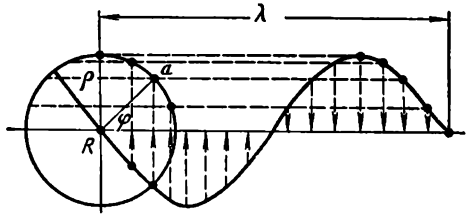


Fig. 257. Harmonic vibration

Let us imagine a point a travelling at a uniform velocity along the circumference of radius R.

Having drawn two mutually perpendicular diameters of the circle, we project the point a onto one of these diameters, in this case the

vertical one, and obtain a point p. At a uniform velocity of the point a along the circumference, the velocity of its projection, i.e., of the point p, will not be uniform. The velocity of the point p is highest at the centre and decreases upwards and downwards from the centre, dropping to zero at the intersection of the circumference with the vertical diameter.

By plotting a curve showing the nature of variations in the velocity of the point p, we obtain a sinusoid. It shows the velocity of the point p at given moments.

If instead of velocity of the point p we take the tension of an electric or magnetic vector at a given moment, the sinusoid will present a vivid picture of the state of these tensions at that moment. The angle which defines the position of the point a on the circumference and,

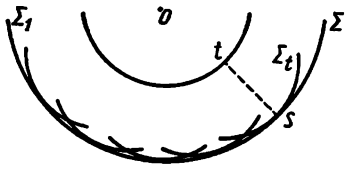


Fig. 258. Plotting a spherical wave

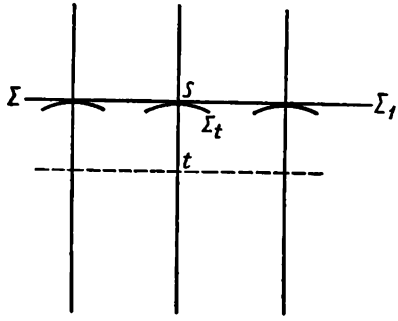


Fig. 259. Plotting a plane wave

consequently, the state of the vibration at a given moment, is called the *phase of vibration*. The distance λ between the two nearest corresponding points of the sinusoid is called the *wavelength*. The distance travelled by a ray of light in one second in a vacuum is the velocity of light V_0. When we divide this distance by the wavelength we obtain

$$\frac{V_0}{\lambda} = \nu.$$

The value thus obtained is the *frequency of vibration*. The colour of light depends on the wavelength λ, its brightness depends on a value R which is called the *amplitude of vibration*, brightness being proportional to the square of the amplitude.

According to the Huygens theory, when light waves pass into an optically isotropic medium, any points that are removed from the initial point of vibration by the same number of waves can be regarded as new initial points of vibration. In order to determine the direction of a ray it is necessary to plot the front of an elementary wave, Σ_t, near each new initial point (t in Fig. 258). Then a front $\Sigma\Sigma_1$ should

be drawn which is tangent to all these fronts; it is known as the directional front. The lines connecting the initial vibration points and the tangent points will be the directions of rays (tS in Fig. 258). If the initial point of vibration is infinitely removed, the rays will be parallel and the light will be propagated in plane waves (Fig. 259).

In an isotropic medium a normal to the tangent curve coincides with the direction of a radius drawn towards the tangent point.

PROPAGATION OF LIGHT IN AN OPTICALLY ANISOTROPIC MEDIUM

Here we have a picture entirely different from that of propagation in an isotropic medium. The front of the light wave is not spherical, but more complicated in form.

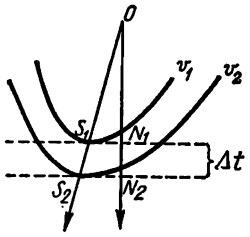


Fig. 260. Propagation of light in anisotropic medium

Therefore, the directions of wave propagation (normals) in most cases do not coincide with the direction of the rays.

If a light wave in the form of an ellipsoid originates at point O (Fig. 260) located in an optically anisotropic medium, the ray OS_1 will not coincide with the direction ON_1 of the normal to the wave, as can be seen from the drawing. In a given period of time, Δt, the wave will travel from the position v_1 to the position v_2. As $S_1S_2 \neq N_1N_2$, the velocities of the rays and the normals in an anisotropic medium are not similar.

As the human eye receives its light impressions from waves, we shall hereafter refer to the phenomenon in terms of waves. Conventional constructions of geometrical optics are valid for waves, but not for rays.

POLARIZATION OF LIGHT AND THE WAVE FRONTS CHARACTERISTIC OF THE OPTICAL PROPERTIES OF CRYSTALS

The vibrations of the tensions of the electric and magnetic vectors always remain perpendicular to the direction of propagation of a light wave, but they may be continually changing their position in space. This property is characteristic of ordinary or "natural" light. In other cases the trajectory of vibrations remains constant and may be in the form of a curve or a straight line. In such cases we deal with *polarized* light.

Fig. 261 shows a cross-section perpendicular to the direction of propagation of a light wave. Tensions of one of the vectors are denoted by the arrows. Fig. 261, *a* shows that the position of the vectors is

constantly changing. Fig. 261, *b* shows that all vibrations are in the same plane.

The vibrations of the electric and magnetic vectors are in two mutually perpendicular planes. For better illustration we have taken a case where the trajectories of vibrations are straight lines, and their sum determines the position of a plane which is parallel to the propagation of the wave. In this case we have *plane polarized* light. When the trajectory is circular or elliptical the polarization is called *circular* or *elliptical*.

Ordinary light becomes partly polarized on reflection and refraction, and completely polarized on passing through an optically anisotropic medium. Since a crystalline medium is in the overwhelming majority of cases optically anisotropic (except for the crystals of the cubic system), we shall have to deal mainly with polarized light.

In passing from one medium (air) to another (glass) a light wave is reflected and refracted. In a reflected wave (Fig. 262), some of the wave vibrations are polarized in a plane perpendicular to the plane of incidence. A refracted wave is supplemented by vibrations in the plane of the diagram, i.e., parallel to the plane of incidence. The degree of this partial polarization of the reflected and refracted waves depends on the angle of incidence and the refractive indices of the two media. Multiple repetition of the phenomenon results in an increased percentage of polarized vibrations.

The most favourable angle of incidence, i.e., one at which the two waves are almost completely polarized, is the angle whose tangent is equal to the refractive index of glass, if the first medium is a vacuum or air.

On entering an optically anisotropic crystalline medium an ordinary light wave is resolved into two plane polarized waves, their planes of vibration being mutually perpendicular. These waves have different properties and names.

Let us first look at the case of crystals related in their external form to intermediate systems, i.e., to trigonal, tetragonal, and hexagonal systems. On entering such a crystal an ordinary light wave is resolved into two plane polarized waves, the first of which propagates with the same velocity in all directions, i.e., has a constant refractive index. This wave similar to a spherical one in an optically isotropic medium (but polarized) is called an *ordinary* wave and is denoted by *o* or ω. The velocity and consequently the refractive index of the other wave vary with change of direction. An ellipsoid of rotation is the characteristic shape of the propagation front of this wave, which is called an *extraordinary* wave and is denoted by *e* or ε.

Let us in turn look at the nature of propagation of the two waves originating at a luminous point in an optically anisotropic medium with variable relative velocities of propagation.

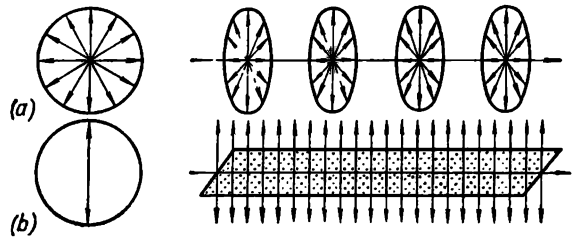


Fig. 261. Vibrations in an ordinary and a polarized waves

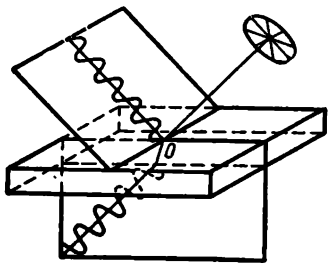


Fig. 262. Polarization by reflection and refraction

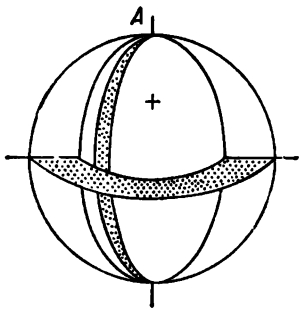


Fig. 263. Wave fronts in a positive uniaxial crystal

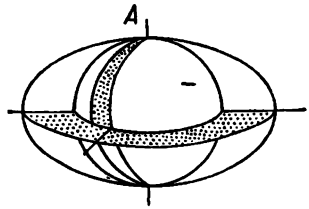


Fig. 264. Wave fronts in a negative uniaxial crystal

Insofar as we have here two different waves, we should obtain double surfaces inscribed one inside the other. The velocity of the ordinary wave may be either higher or lower than that of the extraordinary one. In the first case we have a sphere with an ellipsoid of rotation inscribed in it (Fig. 263), in the second case—an ellipsoid of rotation with a sphere inscribed in it (Fig. 264). In both cases the fronts come into contact at two diametrically opposite points. The velocities of the two waves are identical in the direction of A defined by these points. In other words, there is no birefringence in this direction, which is called an *optic axis.*

In the above cases there is only one such direction, therefore crystals of the trigonal, tetragonal, and hexagonal systems are optically *uniaxial.* When the velocity of the ordinary wave is higher than that of the extraordinary one (Fig. 263), the crystal is considered to be *optically positive* (+); when it is lower (Fig. 264), the crystal is *optically negative* (—). The circular cross-section is always normal to the optic axis, as this axis coincides with the axis of rotation of the ellipsoid.

Now let us look at another group of optically anisotropic media: crystals of the lower systems—orthorhombic, monoclinic, and triclinic. On entering these crystals an ordinary light wave is also resolved into two waves polarized in two mutually perpendicular planes. However, we are not dealing with ordinary waves, as in the case of uniaxial crystals, because they do not propagate along a spherical front, but along a complex front of a higher order. The two fronts intersect at four points, the lines connecting pairs of points being optic axes. Thus, we have two optic axes here, A_1 and A_2, hence all crystals of the lower systems are called *optically biaxial.*

Fig. 265 shows the wave front of a biaxial crystal. Its principal sections are given in Fig. 266.

For plotting wave fronts an imaginary surface can be used, a so-called *Fresnel ellipsoid,* which is of a given shape for each substance and is definitely oriented with respect to the symmetry elements of crystals. In order to determine the velocities of the two waves in the direction OS (Fig. 267), a cross-section of the Fresnel ellipsoid through the centre and perpendicular to OS must be drawn. The dimensions of the semiaxes of the cross-sectional ellipse give the velocities of the two waves in the direction OS. Plotting the lengths of the semiaxes from the centre on the line OS, we obtain points facilitating the construction of the wave fronts.

If in our construction we make use not of the wave velocities but of the actual refractive indices, and plot them in the direction of the corresponding waves building from them a figure, we shall obtain not a double surface but an ellipsoid which is called an *optical indicatrix.*

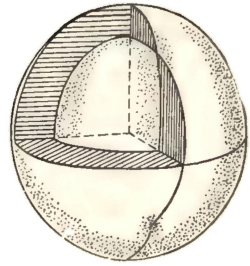


Fig. 265. Wave front in a biaxial crystal

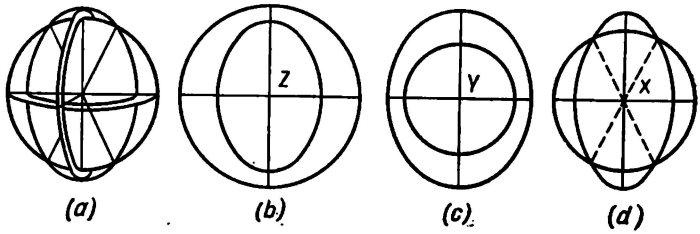


Fig. 266. Principal cross-sections of the wave front in biaxial crystals:
(a) mutual arrangement of principal cross-sections; (b) cross-section perpendicular to Z axis; (c) cross-section perpendicular to Y axis; (d) cross-section perpendicular to X axis

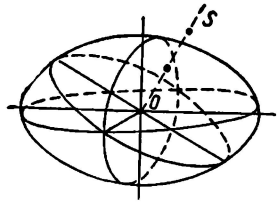


Fig. 267. Fresnel ellipsoid

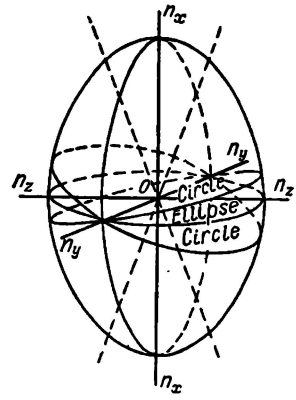


Fig. 268. Indicatrix cross-sections in a biaxial crystal

The indicatrix of optically isotropic crystals of the cubic system is in the shape of a sphere.

In optically uniaxial crystals of the intermediate systems the indicatrix has the form of an ellipsoid of rotation elongated in the direction of the optic axis in positive crystals ($n_e > n_o$), and oblate in negative crystals ($n_o > n_e$). The difference between n_o and n_e is called the *strength*, or the *value*, *of double refraction* (birefringence) and is designated by R.

In the lower systems the optical indicatrix has the form of an ellipsoid with three unequal axes. The semiaxes of its three principal sections are given by the refractive indices, n_x—maximum, n_y—intermediate, and n_z—minimum. An ellipsoid with three unequal axes has two circular sections which are perpendicular to the optic axes. To check the truth of this statement let us analyse the following construction (Fig. 268).

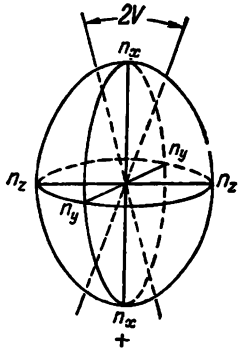


Fig. 269. A positive biaxial crystal

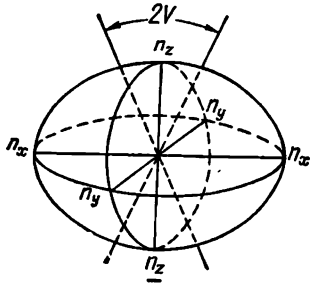


Fig. 270. A negative biaxial crystal

In an ellipsoid, shown diagrammatically, the maximum refractive index, n_x, is arranged vertically, the minimum, n_z, horizontally from left to right, and the intermediate, n_y, also horizontally, but rotated to the left and slightly inclined downwards. The three principal sections are ellipses.

Let us look at two of them: the first passing through n_x and n_y and the second connecting n_y and n_z, n_y is a common axis for the two sections. If we draw several more sections always passing through n_y, with the other axis varying from n_x to n_z, we shall inevitably have a section within the right angle $n_x O n_z$ which will have both axes equal to n_y, insofar as $n_x > n_y > n_z$. Such a section will be a circle, and the optic axis must be normal to it.

Insofar as passing from the $n_y n_x$ to the $n_y n_z$ section we can move either to the right or to the left, we obtain two circular sections, which

fact corresponds to the presence of two optic axes. The angle between them is denoted by $2V$ if it lies within th crystal, and by $2E$ if it is found to lie outside of the crystal (in space).

In intersecting, the axes form two pairs of equal angles—a pair of acute angles and a pair of obtuse angles. In very rare cases they are mutually perpendicular, when all the four angles are right angles. The line bisecting the acute angles is called an *acute bisectrix*, and the one that bisects the obtuse angles is an *obtuse bisectrix*. When the acute bisectrix coincides with n_x, the crystals are called optically *positive biaxial* (Fig. 269), and when it coincides with n_z they are called optically *negative biaxial* (Fig. 270).

POLARIZATION OF LIGHT

It has already been said that partial polarization takes place on reflection and refraction of ordinary light. Complete polarization takes place only when light passes through an optically anisotropic crystalline medium. Therefore, crystals have long been used for producing polarized light. However, we are left with a problem as two polarized waves emerge from a crystal, while only one is wanted. The second wave can either be absorbed or removed artificially. Let us analyse both cases.

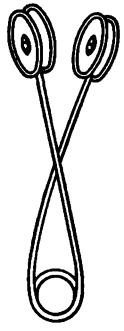


Fig. 271. Tourmaline clips

1. Only one wave will emerge from a crystal if the second wave is absorbed by the crystal matter itself. Green tourmaline crystals are capable of such absorption; this mineral belongs to the ditrigonal pyramidal class of the trigonal system ($L^3 3P$). Tourmaline freely transmits waves with vibrations parallel to its optic axis, and almost completely absorbs vibrations perpendicular to it. Thus, if a lamina of tourmaline is cut parallel to the L^3 axis, a natural polarizer is obtained which transmits only one wave polarized in a known plane.

A useful instrument in the study of optical phenomena in crystals consists of two tourmaline laminae through which light is allowed to pass; it is known as *tourmaline clips* (Fig. 271). Each lamina can be rotated in its holder. The lamina which first transmits light is called a *polarizer*. The other plate, which allows one to examine the wave transmitted by the first plate, is called an *analyzer*. When the two plates are placed parallel to each other, light passes through them unchanged. If the second plate is turned through a given angle, the brightness of light diminishes, reaching zero on rotation through 90°. If the polarizer and analyzer are parallel, the brightness of light is at its maximum, if

they are crossed, the brightness is at its minimum, i.e., complete extinction takes place.

In spite of their simplicity tourmaline clips are not widely used, chiefly because: (1) crystals of perfectly transparent light-green tourmaline of sufficiently large cross-section are relatively rare; (2) the colouring of plates frequently prevents adequate observation of optical phenomena in crystals.

At the present time artificial products, known as *polaroids*, are often used as polarizing plates. These are transparent films containing minute oriented particles of strongly dichroic matter (i.e.,

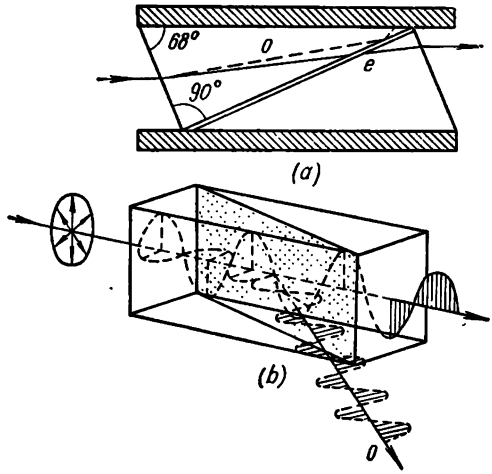


Fig. 272. A Nicol prism:
(a) cross-section; (b) ray path

capable of varying absorption of light in two different planes). Such polaroid films transmit only one polarized wave, and may be made very large. Polaroids are manufactured in large quantities and are used in many different optical instruments.

2. Speaking of polarizing devices in which one wave is eliminated artificially we shall look at a prism invented in 1828 by J. Nicol and named after him.

The Nicol prism (Fig. 272) is made of Iceland spar (calcite, $CaCO_3$). Calcite has $L_6^3 3L^2 3PC$ symmetry; it has perfect cleavage parallel to three planes of a rhombohedron $\{10\bar{1}1\}$, and exhibits very strong birefringence:

$$n_o - n_e = 1.658 - 1.486 = 0.172.$$

The Nicol prisms, which are usually called simply *nicols*, are made of perfectly transparent colourless calcite. An elongated cleavage

parallelepiped is sawn along the short diagonal, the end faces are ground to give a 68° angle, and then the pieces are re-cemented together with Canada balsam.

On entering the prism an ordinary light wave (see Fig. 272) is resolved into two plane polarized waves: an ordinary one, *o*, and an extraordinary one, *e*.

The ordinary wave, whose refractive index in calcite is constant (n_o=1.658) reaches the Canada balsam which has a refractive index of 1.54, suffers total internal reflection, and is absorbed by the blackened prism holder.The extraordinary wave has a variable refractive index of 1.516 in the direction parallel to the long edges of the prism. This wave suffers almost no refraction on passing from the calcite to the Canada balsam and again to the calcite, as 1.516 and 1.54 are fairly close values. Therefore, a single plane polarized extraordinary wave *e* emerges from the nicol (see Fig. 272).

Perfectly transparent and colourless calcite crystals of large size are rare and therefore very expensive. It has been suggested that the price of nicols could be reduced by replacing one of the halves by glass with a refractive index close to that of Canada balsam, n=1.54. Indeed, the removal of the ordinary wave is effected in only one of the prism halves (Fig. 272, *a*, upper left), therefore, the second half of the nicol can be made of cheaper material.

The field of vision of a nicol is limited to 24°.

At present polarizing light filters are often used instead of the Nicol prisms. These are thin drawn out films made of polyvinyl alcohol tinted with iodine. The resulting dichroic polyvinyl-iodine complexes are arranged parallel to the axis along which the film was drawn.

POLARIZING MICROSCOPE

A *polarizing microscope* is one of the most important instruments used in the study of the optical properties of crystals (Fig. 273). Without going into great detail we shall point out the essential features in which it differs from the microscope used in biological work.

Between an illuminating mirror, *S*, and a stage, *T*, is placed a nicol *P* called a polarizer. The nicol can rotate about an axis perpendicular to the plane of the microscope stage.

Inside a tube between the objective, *Ob*, and the eyepiece, *E*, is placed a second nicol *A*—the analyzer. It too can rotate and can be removed from the tube.

The round rotating stage is calibrated and its position can be read off a fixed scale.

Between the polarizer and the stage there is pivoted a condenser *L*—a small lens of large curvature (for obtaining strongly converging beams) which is called the Laseau lens.

Between the analyzer and the eyepiece there is a second sliding lens B—the Bertrand lens which serves as an additional objective for studying phenomena in the main focal plane of the microscope objective.

The lower part of the tube has slots V arranged at an angle of 45° to the symmetry plane of the microscope. These slots serve for introducing a quartz wedge, a gypsum or mica plate, the use of which will be described later.

The eyepiece contains cross hairs.

The objectives are so mounted that they can be aligned with the axis of the microscope.

Non-transparent minerals are examined with what is known as a *petrographic microscope*. It is substantially the same as a polarizing microscope but with a special illumination device—an opaque illuminator, which makes it possible to illuminate from above an object on the stage. The opaque illuminator contains an iris diaphragm, a collimator lens, and a reflecting prism. The analyzer is placed in front, in the inlet tube. The stage of the microscope can be moved up and down, thus eliminating the need for the readjustment of the light source on refocusing.

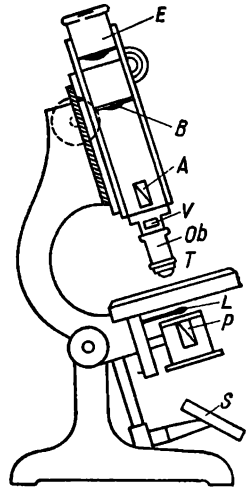


Fig. 273. Polarizing microscope

MEASUREMENT OF REFRACTIVE INDICES

We shall discuss below the three principal methods of determining these highly important optical constants.

Prism Method. This method is based on the measurement of the angle of least deviation.

A crystal, prismatic in shape, is placed on the stage of a one-circle goniometer. Waves of monochromatic light impinge on it from a collimator. In passing through the crystal the wave should pass at right angles to the plane which bisects the refracting angle A of the prism (Fig. 274). In this diagram φ is the angle between the path of the wave within the prism and the plane KF; Δ is the angle of deviation of the ray that has passed through the prism; i, i', r, r' are angles of incidence and the corresponding angles of refraction. The refractive index in the direction MP we shall call n.

In accordance with the law of refraction

$$\sin i = n \sin r, \quad (1)$$

$$\sin i' = n \sin r'. \quad (2)$$

From the triangle MPR whose external angle is A we have

$$r+r'=A. \tag{3}$$

From the triangle MPQ whose external angle is Δ and from the equation (3) we have

$$i+i'=A+\Delta. \tag{4}$$

From the triangle KFP whose external angle is φ we have

$$\varphi=90^\circ-r'+\frac{A}{2}=90^\circ+r-\frac{A}{2}=90^\circ+\frac{r-r'}{2}. \tag{5}$$

We have five equations with eight unknowns. It is essential to determine three of them in order to calculate the others.

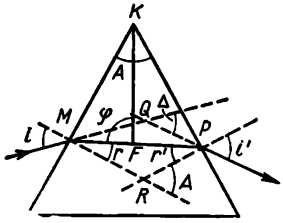


Fig. 274. Ray path in the determination of refractive index by the prism method

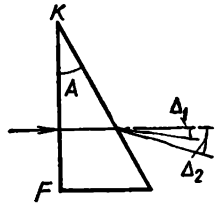


Fig. 275. Ray path in the determination of refractive index by the semi-prism method

The least angle of deviation of a refracted wave can be found by rotating a prism about an axis which is parallel to its edges. In this case the rays within the prism will be perpendicular to the plane which bisects the angle A. The angle φ is 90° in this case, and consequently, $i=i'$ and $r=r'$; therefore,

$$n=\frac{\sin\frac{A+\Delta}{2}}{\sin\frac{A}{2}}.$$

The formula is simplified if the prism is cut along the plane KF (Fig. 275) and the wave entering the crystal is directed normally to KF. Then

$$n_1=\frac{\sin(A+\Delta_1)}{\sin A},$$

$$n_2=\frac{\sin(A+\Delta_2)}{\sin A},$$

where n_1 and n_2 are refractive indices of the two waves.

For rapid determination of the three principal refractive indices (in biaxial crystals) the prisms should be so orientated that the *KF* plane is parallel to one of the three symmetry planes of an ellipsoid. In the general case three prisms should be made. For uniaxial crystals it will suffice to have one prism with edges parallel to the optic axis in order to determine the refractive indices for ordinary and extraordinary waves.

Refractometer Method (Method of Total Internal Reflection). A *VC* wave (Fig. 276) can pass from medium *I* into medium *II*, which has a smaller refractive index, only if the angle of refraction, *i*, is less than 90°, otherwise the wave will be totally reflected back into medium *I*. If we regard *KC* as an incident wave, and *VC* as a refracted one, the limiting angle *R* will be the angle of total internal reflection.

If we cut a plate out of the crystal under study, parallel to one of the symmetry planes of the optical indicatrix, and place the plate on a glass hemisphere (Fig. 277) with a very high refractive index (*N*), we shall be able to determine two of the principal refractive indices of the crystal.

If the refractive index of the glass is denoted by *N*, and the relative refractive index at the point where the ray passes from crystal to glass by *n'*, we shall have

$$N = n \cdot n',$$

where *n* is the unknown refractive index at the point where the ray passes from crystal to air.

Hence,

$$n' = \frac{1}{\sin R},$$

$$n = N \sin R.$$

If the incident light is directed approximately parallel to the plane surface of the hemisphere (Fig. 278), we shall be able to observe a distinct boundary in the field of vision of the tube *F*, corresponding to the direction of the wave *3* which travels within the glass at an angle of total internal reflection. One half of the field of vision is dark, the other half is illuminated by waves travelling along directions *4*, *5*, *6*, etc.

If the incident light is directed through the hemispherical surface, we obtain the image shown in Fig. 279.

Knowing *N* and having measured the angle *R* we can determine the unknown refractive index with the aid of the above equation.

The instrument used for this purpose is called a *crystal refractometer.*

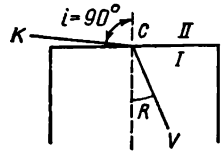


Fig. 276. Ray path in the determination of refractive index by the method of total internal reflection

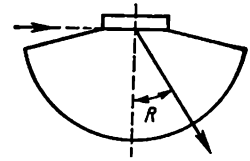


Fig. 277. Hemisphere with a crystal plate

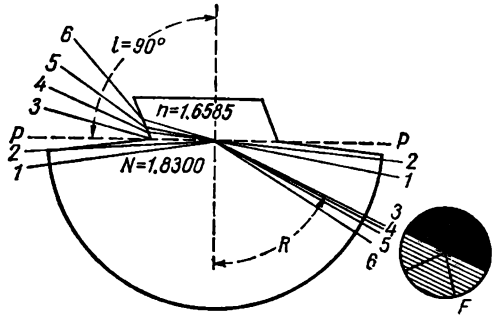


Fig. 278. Ray path in a refractometer when incident rays are parallel to the plane surface of the hemisphere

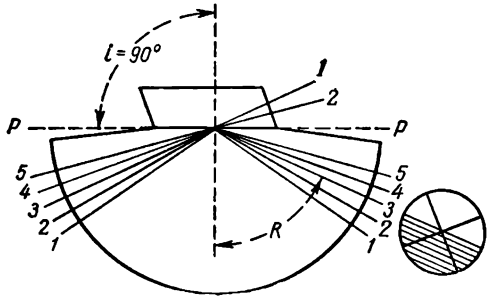


Fig. 279. Ray path in a refractometer when rays pass through the hemisphere

If a crystal plate is sufficiently thick and has been cut so that it has a face parallel to one of the principal sections of the indicatrix, all the three refractive indices of a biaxial crystal can be determined.

The disadvantage of this method is that it cannot be used for the determination of very high refractive indices, as they must always be less than N—the refractive index of the glass hemisphere. In modern instruments the latter is about 1.8-1.9.

Immersion method is based on two phenomena:

(1) a transparent colourless crystal (or a fragment of it) immersed in a liquid with the same refractive index becomes invisible;

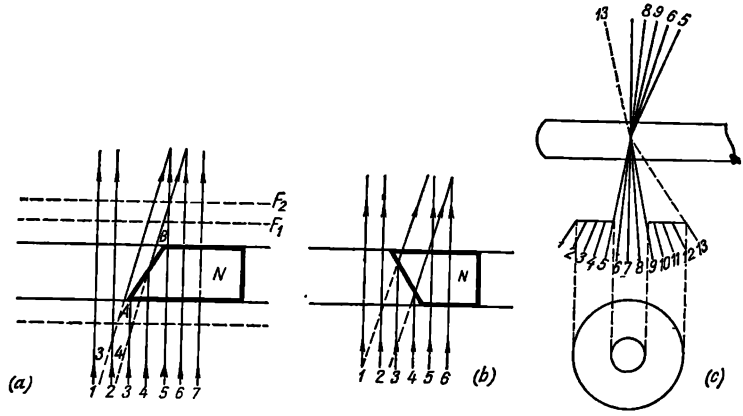


Fig. 280. Development of the Becke line

(2) if the liquid and the crystal have different refractive indices, a light line called the *Becke line* will appear at the boundary between them. This can be explained in the following way.

Let us imagine that we have in the field of vision of the microscope two contacting media which have different refractive indices N and n. Both media may be solid, or one of them may be liquid. If N is greater than n, we shall observe the following at the boundary between them. A bundle of parallel rays from the polarizer impinges on our object from below (Fig. 280, *a*).

The interface of the two media—a crystal and a liquid or two crystals—may have one of the following three shapes:

(1) the crystal with the higher refractive index will appear as a wedge with the lower face longer (Fig. 280, *a*);

(2) the same crystal will appear as a wedge with the upper face longer (Fig. 280, *b*);

(3) the crystal does not expand and its boundary remains perpendicular to the plane of the object under investigation (Fig. 280, *c*).

In the first case the rays numbered *1*, *2*, *5*, *6*, *7* will pass unrefracted. The rays *3* and *4* will deflect towards the base of the prism obtained as a result of the expansion. Therefore, the edge of a crystal with a higher refractive index will be illuminated more intensely. If we raise the microscope tube, we shall move the focus from position F_1F_1 to position F_2F_2, and the more strongly illuminated edge of the crystal (Becke line) will move towards the substance with the higher refractive index.

In the second case (Fig. 280, *b*) the rays *3* and *4* will refract towards the base of the prism and will also illuminate more intensely the edge of the more strongly refracting crystal.

In the third case (Fig. 280, *c*) when the boundary is perpendicular to the plane of the object, there will be no refraction of the parallel rays. But in addition to the parallel rays there are always some inclined rays. The rays *1-5* impinging upon the boundary between the substances N and n with the lower index (since they come from the medium n) will enter the N crystal. But the rays from N impinging on the same boundary will undergo total internal reflection (rays *8* and *9*), and the edge of a substance with a higher refractive index will be illuminated more strongly.

When the microscope tube is raised, the Becke line will travel in the former direction.

To have rays impinge on an object at a slight angle it is necessary to pass the bundle of rays through a diaphragm and to lower the polarizer as much as possible.

The examination is made with a polarizing microscope. A crystal or its fragment is ground in a mortar; a small quantity of the powder is placed on a slide, and a drop of liquid with a known refractive index is added. This is then topped with a cover glass.

When the refractive indices of the liquid and the crystal are the same, the grains of the latter become invisible. If the indices are not the same, the Becke lines will appear round the edges of individual grains.

If the microscope tube is slightly raised by means of an adjusting screw, the Becke line will move towards the medium with the higher refractive index. Thus, if the line moves into the crystal, it means that the refractive index of the crystal is higher than that of the liquid; if the line moves into the liquid, the refractive index of the latter is higher.

When there is a sufficient choice of liquids with different known refractive indices, the refractive index of a crystal can be determined with sufficient accuracy. If, for instance, we have selected two liquids one of which has a refractive index, n_1, higher, and the other,

n_2, lower than that of the crystal, the refractive index of the latter, N, will be

$$N = \frac{n_1 + n_2}{2}.$$

A good working set consists of 80-100 liquids with refractive indices from 1.3 to 1.8, the difference between the indices of adjacent liquids being 0.003-0.007.

Liquids which are often used in determining the refractive indices of crystals by the immersion method are listed in Table 14, N being given for a wavelength of 0.589 μ.

Table 14

Liquid	N	Liquid	N
Methyl alcohol	1.33	Nitro-benzene	1.554
Water	1.333	Aniseed oil	1.56
Ethyl alcohol	1.36	Monobromobenzene	1.561
Hexane	1.39	Aniline	1.58
Amyl alcohol	1.40	Bromophorm	1.590
Chlorophorm	1.45	Almond oil	1.60
Carbon tetrachloride	1.466	Cinnamon oil	1.605
Glycerine	1.47	Monoiodinebenzene	1.621
Castor oil	1.48	Carbon sulphide	1.63
Xylene	1.49	α-Monochloronaphthalene	1.639
Benzene	1.501	α-Monobromonaphthalene	1.658
Cedar oil	1.516	α-Monobromonaphthalene and methylene-iodide	1.70
Monochlorobenzene	1.527		
Ethylene bromide	1.536	$KHgI_3$	1.73
Creosote	1.54	Methylene-iodide	1.74
Clove oil	1.544	Solution of sulphur in methylene-iodide	1.800

INTERFERENCE OF LIGHT WAVES IN CRYSTALS

We shall examine some phenomena of light occurring in crystal plates under the microscope.

A plane polarized wave emerging from the lower nicol on entering a crystal is resolved into two waves with mutually perpendicular planes of vibrations. On entering the analyzer each of these waves breaks up into components in accordance with the rule of the parallelogram. The upper nicol transmits only that wave component which can pass through it.

We shall thus observe the result of addition of two waves whose vibrations are made to coincide in the same plane by the analyzer; in other words, we shall observe the phenomenon of interference, the

nature of which depends on several factors; (1) thickness of the crystal plate; (2) direction of the plate section with respect to the indicatrix; (3) orientation of the crystal with respect to the nicols; (4) position of the nicols with respect to each other; (5) nature of the light emerging from the mirror.

Let us analyse these factors in greater detail with reference to a beam of parallel rays thrown by the mirror.

In passing through the crystal k (Fig. 281) the two waves, W_1 and W_2, which have developed in it, have a phase difference R. The waves have different refractive indices and therefore pass through the crystal

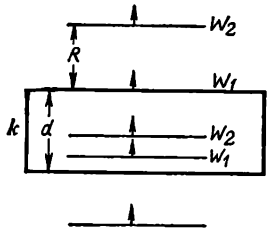


Fig. 281. Phase difference between two waves

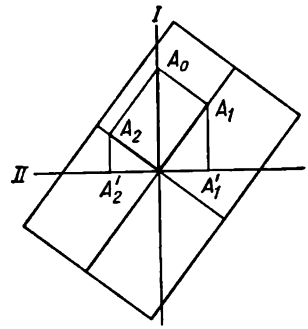


Fig. 282. Interference in parallel light

at different velocities. Consequently, one of the waves slightly outruns the other. Denoting the refractive indices of the two waves by n_1 and n_2, and the thickness of the plate by d, we obtain

$$R = d(n_1 - n_2).$$

Hence, the phase difference depends on the thickness of the plate and on the strength of birefringence of the crystal in a given direction, i.e., it depends on the orientation of the plate with respect to the indicatrix.

If the polarizer and analyzer transmit vibrations in the directions I and II (Fig. 282), the amplitude, A_0, of the waves entering the crystal will be resolved into two component amplitudes, A_1 and A_2.

In order to determine the brightness of light for the waves which have passed through the analyzer II, we have to resolve each of the amplitudes (A_1 and A_2) so that one component is parallel to the plane in which the vibrations are transmitted by the analyzer, and the other is perpendicular to it. Two waves with amplitudes A'_1 and A'_2 will then pass through the analyzer. Their interference will be observed under the microscope in the from of interference colours.

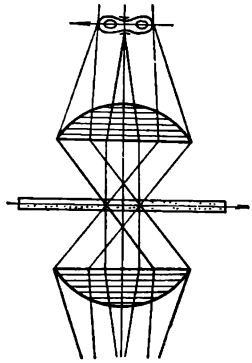


Fig. 283. Interference in convergent light

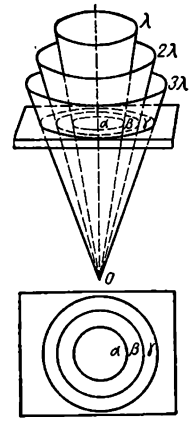


Fig. 284. Wave cones in a uniaxial crystal

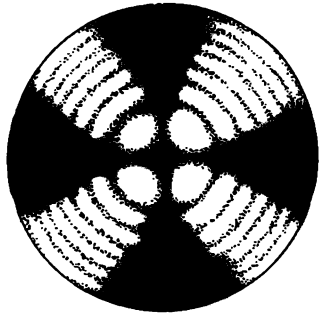


Fig. 285. Uniaxial interference figure in convergent light

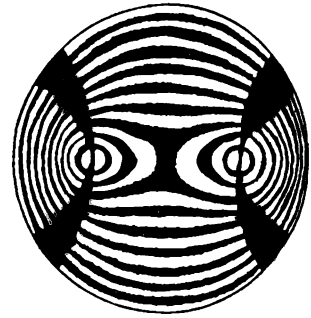


Fig. 286. Biaxial interference figure in convergent light

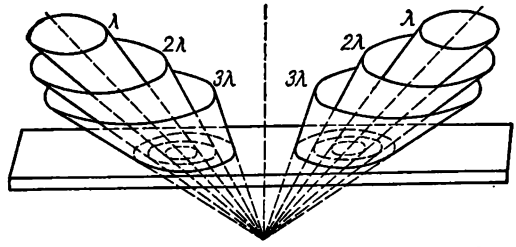


Fig. 287. Wave cones in a biaxial crystal

During a complete revolution of the stage with the crystal the plate will turn dark four times. In other words, there will be four extinction positions, in which the vibration planes of the waves generated in the crystal plate coincide with the vibration planes of the crossed nicols. The crystal will attain maximum brightness for times (in diagonal positions with respect to the nicols, i.e., at angles of 45° to the nicols).

Between parallel nicols the colour is complementary to that observed with crossed nicols.

With monochromatic light it is only the brightness that changes. With white, or polychromatic, light the intensity of the interference colours changes at different angles of rotation.

An entirely different type of image is observed in light converging at a large angle, which is obtained by insertion of a Laseau lens under the microscope stage, i.e., between the polarizer and the crystal.

In each individual section the two oblique waves (Fig. 283) travel with unequal velocities and, on interference, produce a series of curves which are dark and light in monochromatic light and tinted with interference colours in white light. This phenomenon can be observed upon removal of the eyepiece or upon insertion of the Bertrand lens which makes it possible to see the magnified (with the eyepiece in place) image lying in the main focal plane of the microscope objective.

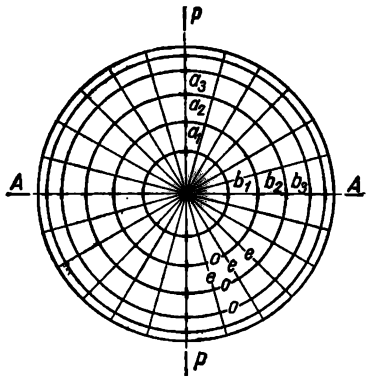


Fig. 288. Direction of wave vibrations in a uniaxial crystal

Optically uniaxial and biaxial crystals produce entirely different images in convergent light. In the first case, with crossed nicols, a dark cross cutting a number of concentric rings lying in the field of vision will be observed on sections cut perpendicularly to the optic axis (Figs. 284 and 285). The arms of the cross are parallel to the vibration planes of both nicols. The optic axis emerges at the intersection point of the arms of the cross.

Sections of biaxial crystals cut perpendicularly to the acute bisectrix produce the image shown in Figs. 286 and 287. In the field of vision we observe curves which are called *Cassini rings* and are intersected by two dark hyperbolae called *isogyres*. Between parallel nicols the arms of the cross and the isogyres become light.

The appearance of the dark and light crosses and isogyres may be explained as follows. The two waves generated in the crystal vibrate in two mutually perpendicular planes. For uniaxial crystals this can be represented diagrammatically as shown in Fig. 288.

Vibrations of the extraordinary wave propagate along the radii, and those of the ordinary one, along the tangents. If the nicols (*PP*, *AA*) are crossed, the waves from the polarizer vibrate only along the radius (*PP*) at the points a_1, a_2, a_3, etc., and cannot pass through the analyzer. Therefore, we have dark patches at the points a_1, a_2, a_3, etc.

Vibrations parallel to *PP* and travelling along the tangents could pass through the points b_1, b_2, b_3, etc., but they are arrested by the analyzer placed in the position *AA*. Therefore, at the points b_1, b_2, b_3, etc., we shall also have dark patches.

Waves with vibrations perpendicular to *PP* are not arrested by the analyzer between parallel nicols, and the resulting cross is bright.

As one extraordinary wave passes through the points a_1, a_2, a_3, etc., and one ordinary wave, through b_1, b_2, b_3, etc., there will be no interference at these points and the arms of the cross will be bright.

SIMPLEST METHODS OF DETERMINING OPTICAL CONSTANTS OF CRYSTALS

Suppose we have a thin plate (a section 0.02-0.03 mm thick) of a rock consisting of numerous tiny crystals oriented at random. We must find such crystal grains in the plate which are favourably oriented for optical examination. We can determine in convergent light whether the crystal is uniaxial or biaxial. This enables us to identify its system from the character of extinction.

We select a section with clear edge lines or cleavage fractures and rotate our object with the help of the microscope stage. If the section plane coincides with the symmetry plane of the indicatrix, extinction will appear when one of the edges is parallel or perpendicular to the eyepiece cross hairs, i.e., we have a case of direct extinction. If the extinction angle is neither 0° nor 90°, the extinction is oblique. The position of both nicols should be previously checked, of course, for coincidence of the *PP* and *AA* planes with the cross hairs.

Optically isotropic crystals belong to the cubic system.

Uniaxial crystals have direct extinction. When symmetrical extinction is observed at an angle of 45°, the crystals belong to the tetragonal system, if the extinction angles are 30° and 60°, they belong to the hexagonal system.

Of the biaxial crystals those belonging to the orthorhombic system have direct, or symmetrical, extinction; crystals of the monoclinic system have mixed extinction, i.e., both direct and oblique. Triclinic crystals produce oblique extinction in all directions.

The optic sign of a crystal is determined with the aid of special wedges or plates inserted in the slots in the microscope tube between the objective and the analyzer (*V*, Fig. 273).

Let us now consider a *quartz wedge* (Fig. 289) and a gypsum plate. The wedge is cut and ground so that the optic axis of quartz is parallel to the shorter side of the plate; the wedge angle is about 1/2°. The lower plane of the wedge is oriented with respect to the quartz indicatrix in such a manner that the n_x axis lies across the wedge, and the n_y axis is parallel to the longer side. Inserting the wedge into the microscope tube slot we can observe the interference colours which

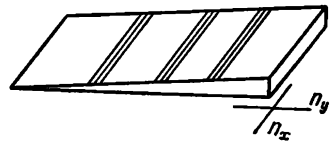


Fig. 289. Quartz wedge

will vary as the wedge is pushed in further and further. As the thickness of the quartz increases the lag of one wave behind the other will also increase, i.e., the phase difference, R, of the two waves will increase.

In the field of vision we shall see interference colours differing in hue and intensity. Colours of several orders are distinguishable depending on the value of the phase difference between the waves. With an increase in the phase difference, R, the order of colours increases.

Colours of the first order are very bright and intense, and those of very high orders (sixth, seventh) are progressively paler and more difficult to distinguish.

The quartz wedge produces the following colours of the first order (Table 15).

Table 15

Phase difference, mμ	Colours of the first order	
	with crossed nicols	with parallel nicols
0	Black	White
100	Grey	Light yellow
260	White	Red
300	Yellow	Violet
450	Brownish	Light blue
500	Orange	
550	Red	Light green

The quartz wedge can be used in determining the optic sign of uniaxial crystals if it is not known whether their habit is prismatic or platy.

If a prismatic crystal is placed under the microscope and the quartz wedge is inserted parallel to its longer side, an increase or decrease in interference colours can be observed. Knowing that the n_z axis of quartz is parallel to the longer side of the wedge, it is possible to tell from the colour variations whether the axis of the higher degree is n_z or n_x. In the first case the colours will increase, hence the optic sign of the crystal is negative ($n_o > n_e$). In the second case the colours will decrease down to total compensation, in which case the optic sign of the mineral is positive ($n_e > n_o$).

An *oriented* cleavage *plate* of gypsum or mica can be used instead of a quartz wedge. Such plates are made more easily, but the advantage of the wedge is that total compensation of the phase difference can be obtained by adjusting the wedge in the slot.

A gypsum plate is used as follows. In a thin section we select a crystal which is oriented so that its section is perpendicular to the optic axis. A Laseau lens is inserted to produce convergent light. A conoscopic image is obtained in the field of vision consisting of a series of concentric circles with a dark cross superimposed. A gypsum plate (a gypsum being optically positive) is inserted in the slot *V* of the microscope tube. The plate by itself usually shows red interference colour of the first order. With an increase in phase difference the colour is increased and red turns to blue, while with a decrease in it the colour turns yellow. Fig. 290, *a* and *b*, shows the orientation of ellipsoids in a gypsum plate and in optically positive (*a*) and negative (*b*) crystals. Colours increase when orientations coincide, and decrease when they are opposite. Therefore, in the quadrants *I* and *III* we shall have blue, and in the quadrants *II* and *IV*— yellow, if the crystal is optically positive. The reverse will be observed with an optically negative crystal, i.e., the quadrants *I* and *III* will be yellow, and the quadrants *II* and *IV*—blue (Fig. 290, *c*, *d*).

DISPERSION OF OPTIC AXIAL ANGLE AND OF BISECTRICES

Insofar as waves of different length have different refractive indices, the optical indicatrix is of different shape for different colours in the same crystal medium.

In individual cases the symmetry elements of an indicatrix and a crystal may or may not coincide.

In orthorhombic crystals the plane of the optic axes is fixed but it may turn abruptly through 90°. The optic axial angle will have a different value for different wave lengths. This phenomenon is called the *dispersion of the optic axial angle.*

In Fig. 291, *a*, the axes for all colours are in the same plane. In Fig. 291, *b*, the axes for different colours are in two mutually perpendicular planes.

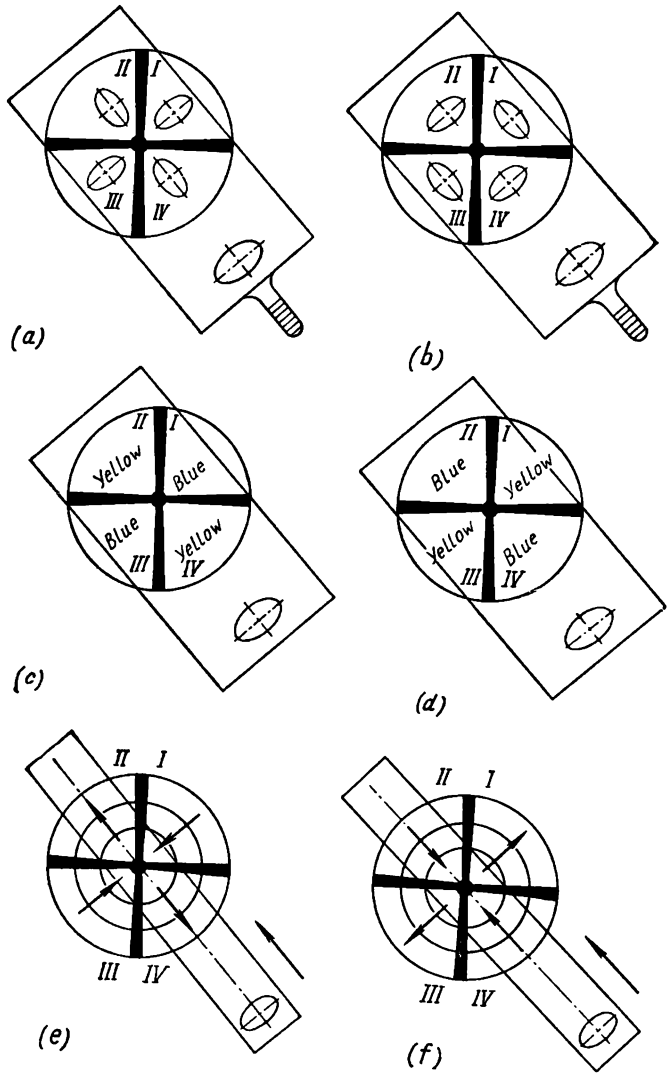


Fig. 290. Determination of optic sign for uniaxial crystals

Let us, for example, denote the angle for violet waves by $2V_v$ and for red ones by $2V_r$. Two cases are possible here: $2V_v > 2V_r$, and $2V_v < 2V_r$. Some crystals show considerable dispersion. For instance, rubidium sulphate has $2V_r = 28°30'$ and $2V_r = 47°30'$. In some cases, such as brookite and goethite, the indicatrix axes for different colours lie in different planes (Fig. 291, *b*).

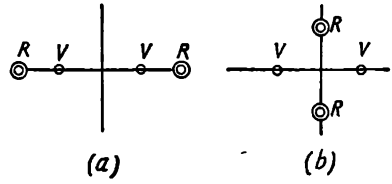


Fig. 291. Dispersion of optic axes

In monoclinic crystals one of the principal axes of the indicatrix for any colour must coincide with the crystallographic axis *II*. The other two axes of the indicatrix may occupy any position provided all the three axes are mutually perpendicular. The non-alignment of the principal axes for different colours is called the

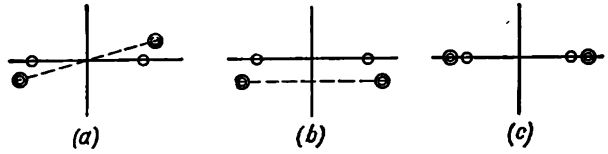


Fig. 292. Dispersion of bisectrices

dispersion of bisectrices. Here we also distinguish several kinds of dispersion: crossed, horizontal, and inclined (Fig. 292, *a*, *b*, *c*).

In triclinic crystals we have the most general case—asymmetrical dispersion.

ABSORPTION OF LIGHT IN CRYSTALS

Some absorption of light takes place even in crystals which seem entirely transparent. In optically isotropic crystals the degree of absorption does not depend on the direction and the absorption surface has the form of a sphere.

In optically anisotropic media the colouring of a crystal depends on the direction of vibrations of the two waves, and the degree of absorption varies with the direction. Therefore, the colouring of a crystal varies with the angle of rotation of the microscope stage. This pheno-

menon is called *pleochroism*. This term describes the ability of crystals for absorbing light to a varying degree depending on the vibration direction of transmitted light waves. In some crystals pleochroism is very pronounced, and in others barely noticeable, so that it can be detected only by very accurate colour analysis. Crystals of the cubic system, being isotropic, have no pleochroism.

The presence of three characteristic colours is called *trichroism*, and the presence of two, *dichroism*. Tourmaline is a good example of a dichroic crystal.

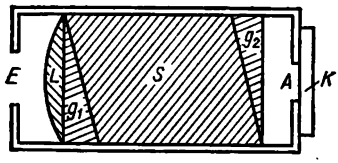


Fig. 293. Haidinger magnifying glass

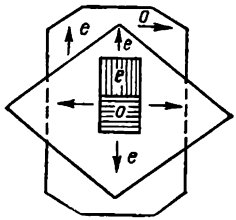


Fig. 294. Aperture in the Haidinger magnifying glass

Pleochroism can be observed under the microscope with the upper nicol removed, i.e., *with the polarizer alone*, as otherwise the interference colours make observation more difficult.

A special dichroscopic Haidinger magnifying glass (Fig. 293) is used for studying the pleochroism of large crystals, for example, gems. It consists of an Iceland spar crystal, S, which is a cleavage fragment in the form of a parallelepiped, and of two glass prisms, g_1 and g_2, which serve to make the prism rectangular. The diaphragm A is square. A magnifying lens L is placed against the prism. A crystal K is placed against the diaphragm A, and the observer looks through the aperture E.

The length of the calcite parallelepiped is so selected as to avoid the overlapping of the images produced by the ordinary and extraordinary waves (Fig. 294).

ROTATION OF THE PLANE OF POLARIZATION

If a plate is cut from a crystal at right angles with an optic axis, it should not produce birefringence and the field of vision between crossed nicols should remain dark. But some crystals show no extinction under these conditions, and to obtain it the upper or the lower nicol must be rotated instead of the crystal.

This phenomenon is caused by rotation of the plane of polarization through a given angle (Fig. 295) during the passage of light through the crystal. To produce extinction the analyzer must be rotated in some cases to the right and in others to the left, which means that crystals may have right-handed and left-handed rotation. As a measure of degree of rotation we take the value of specific rotation, i.e, the angle α through which the polarization plane rotates while the light travels a distance of 1 mm in the crystal.

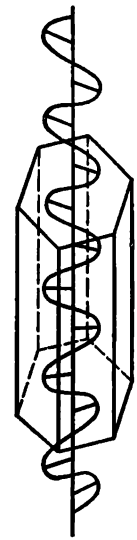


Fig. 295. Rotation of the plane of polarization

The value of specific rotation depends on the length of the light wave and on the substance of the crystal. Short waves produce much greater specific rotation than long ones (see Table 16).

The chemical composition of crystals also strongly affects their rotational capacity. In Table 17 the values of the angle α for a number of minerals are given. These values have been determined for the same wavelength (λ=389.3 mμ) of light.

Cinnabar, HgS, has an α=325° for red colour (λ=686.7 mμ) which is 20 times higher than the rotational capacity of quartz (15°55′ for the same wavelength).

The rotational capacity of crystals is related to the presence of screw axes in their lattices, therefore, only crystals of certain classes have this capacity.

Rotation of the plane of polarization is characteristic not only of solids but also of liquid solutions, e.g., solutions of sugar, which contain carbon molecules with asymmetrical configuration of bonds.

There are special instruments—saccharimeters or polarimeters for determining the concentration of the solution from the degree of rotation produced by the solution of sugar in a cylinder of a given length.

Table 16

Variation of angle α with wavelength for sodium chlorate

Wavelength, λ, mμ	686.7	656.3	589.3	527.0	486.1	430.8	396.9
Angle of specific rotation, α	2°16′	2°30′	3°08′	3°56′	4°40′	6°00′	7°10′

Table 17

Values of angle α for a number of minerals (λ=389.3 mμ)

Mineral	$NaClO_3$	$NaBrO_3$	$KLiSO_4$	SiO_2 (quartz)	$NaIO_4 \cdot 3H_2O$
Angle of specific rotation, α	3°08′	2°10′	3°26′	21°67′	23°18′

FEDOROV METHOD

In examining thin sections of rocks containing a large number of randomly arranged minute crystals it is often difficult to find a crystal grain in an orientation allowing easy measurement of the most important optical constants of the mineral. Locating a suitable grain in a thin section is often time consuming.

To facilitate and speed up this work Fedorov evolved a special method, which was named after him, involving the use of a universal stage (Fig. 296) which is fixed by means of two screws to a microscope stage.

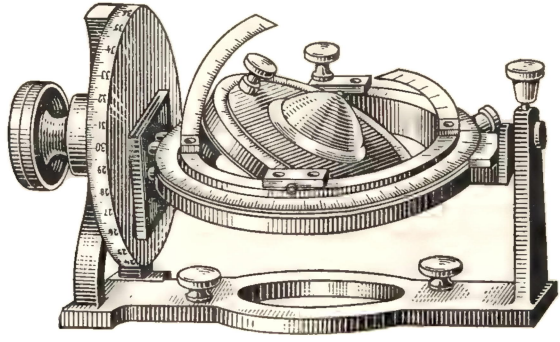


Fig. 296. Fedorov stage

It is evident from the foregoing that optical examination of crystals of some substances under the microscope yields information as to the characteristic properties of these substances which distinguish them from other solids. This is especially true of petrographic study of rock-forming minerals.

A conventional polarizing microscope is, generally speaking, an excellent tool for the purposes of practical crystal optics. It has some defects, however, one of which is the impossibility of rotating a thin

section in any plane but its own. Thus, no matter what mineral grain we choose, we cannot study it in any plane but the one that has been produced incidentally in cutting the section. For this reason, and also for finding the most characteristic directions and planes in a crystal, many grains have to be examined in order to obtain complete optical characteristics of a mineral.

This disadvantage of the polarizing microscope has been considerably overcome at present by the use of the Fedorov universal stage which allows one to rotate an object about four or five axes (instead of one) converging at the centre of the stage.

BRIEF CHARACTERISTICS OF THE OPTICAL PROPERTIES OF CRYSTALS

As regards optical properties all crystals are divided into three groups: (a) optically isotropic (cubic system); (b) optically anisotropic uniaxial (trigonal, tetragonal, and hexagonal systems); (c) optically anisotropic biaxial (orthorhombic, monoclinic, and triclinic systems).

Optically anisotropic crystals produce two light waves polarized in two mutually perpendicular planes.

Each wave has its own characteristic propagation front: a sphere and an ellipsoid for uniaxial crystals, and more intricate fronts—for biaxial crystals.

The fronts of the two waves either come into contact at two points (uniaxial crystals) or intersect at four points (biaxial crystals). These points define the optic axes, i.e., the directions of propagation of light in a crystal without birefringence. Circular sections of ellipsoids are normal to the optic axes.

A front obtained as a result of plotting the refractive indices in the directions of light vibrations is called an *optical indicatrix*. It has the form of an ellipsoid of rotation with a symmetry of $L^{\infty}\infty L^{2}(\infty+1)\,PC$ (for uniaxial crystals), or an ellipsoid with three unequal axes $3L^{3}3PC$ (for biaxial crystals). Crystals are considered optically positive if the optic axis in uniaxial crystals or the acute bisectrix of the optic axial angle in biaxial crystals coincides with the direction of vibration of the wave with the highest refractive index. If these lines coincide with the direction of vibration of the waves with the least refractive index, the crystals are optically negative.

The phenomena of interference of the two polarized waves, observed with the aid of a polarizing microscope in parallel and convergent light, are helpful in determining the most important optical constants and the system of a crystal.

CHAPTER XVI

Other Properties of Crystals

The physical properties of crystals may be divided into two categories: (1) structurally insensitive, and (2) structurally sensitive.

Structurally insensitive properties are those which depend but little, if at all, on a small number of imperfect areas in a crystal. These properties include elasticity, electric conductivity, density, heat conductivity.

The structurally sensitive properties are mechanical strength, internal friction and creep.

Structural imperfections are vacancies in the crystal lattice, foreign atoms, disturbances in the stacking of the layers of material particles, twin boundaries, and dislocations. A dislocation is understood to be a region in which material particles of a crystal lattice have been moved to different distances from their normal position.

MECHANICAL PROPERTIES OF CRYSTALS

Here we shall discuss those physical properties of crystals which are, along with the optical properties, of great practical importance or can serve as essential diagnostic features. These include primarily mechanical properties: cleavage and hardness.

Cleavage is the ability of crystals to split along definite planes. These planes are always parallel to the actual or possible crystal faces, and their position in space can be designated by the same symbols which are used for designating the positions of faces.

What is cleavage due to? Material particles making up a crystal are arranged in space at the nodes of a space lattice or several lattices slid one into another. The forces of cohesion between individual material particles depend on the spacings between them. The closer the particles are to each other, the greater are the forces of cohesion, and vice versa, the greater the distance between the particles, the weaker the forces of cohesion.

Thus, we can formulate the following rule: *the direction of cleavage is parallel to the planes with the greatest reticular density.*

For the sake of simplicity, let us first look at the case of plane nets. Fig. 297 shows that the denser the rows, the greater the distance between the parallel adjacent rows. For instance, $a_1a_2a_3a_4...$ make up a dense row, since the distances a_1—a_2, a_2—a_3, etc., are small. But the rows $a'_1a'_2a'_3...$, $a''_1a''_2a''_3...$ parallel to this row are at a rather large distance from it. The row $a''_1a'_4a_7$ is far less dense, but the parallel rows are much closer to it.

In space lattices plane nets function as rows. Where can we expect splitting to be easiest? Evidently parallel to the faces with the greatest interplanar spacings. In our particular case, if construction is carried out on a plane (see Fig. 297), splitting will be the easiest parallel to the rows $a_1a_2a_3...$, $a'_1a'_2a'_3$, etc.

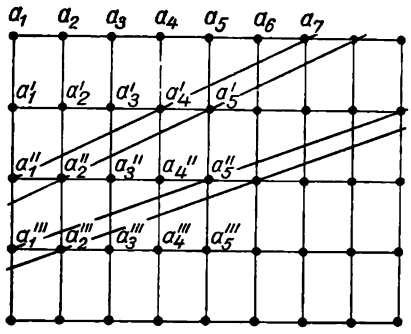


Fig. 297. Different degrees of cleavage on a plane net

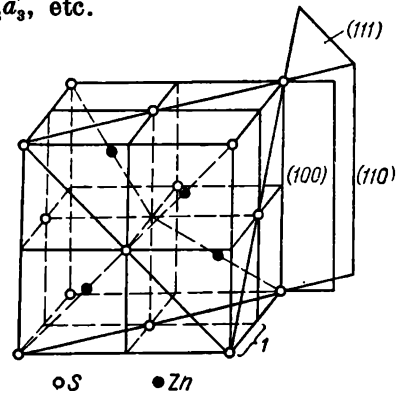


Fig. 298. Different degrees of cleavage in sphalerite (ZnS)

Depending on the structure of the crystal there can be several such directions. Their position and number are directly associated with symmetry.

Wulff showed that in actual crystals cleavage is more complicated, since chemical bonds are added to the forces of cohesion. For instance, in sphalerite, ZnS, (Fig. 298), which belongs to the cubic system, the interplanar spacings (in Å) in the ionic lattice are: 0.500 for the cube (100), if the length of an edge of a small cube (one of the eight cubes into which the unit cell can be broken) is taken to be unity, 0.707 for the rhombic dodecahedron (110), and alternately 0.288 and 0.866 for the octahedron (111).

It would seem here that cleavage would be parallel to the octahedron which has the largest interplanar spacing (0.866). But actually it is parallel to the rhombic dodecahedron where interplanar spacing is 0.707. This is because the layers perpendicular to the octahedron faces consist alternately of ions of zinc and sulphur, while the layers

along the rhombic dodecahedron contain both kinds of ions. In the latter case chemical bonds between adjacent layers are evidently weaker than between layers of the octahedron which consist of ions with different charges (see Fig. 298).

The quality of cleavage is evaluated in accordance with the surface of a split piece, and usually five degrees of cleavage are distinguished: (1) eminently perfect, excellent—the crystal can be split into finest laminae with mirror smooth surfaces (mica); (2) perfect—smooth shiny surfaces (calcite); (3) distinct—smooth surfaces and fractures (feldspars); (4) imperfect—almost no smooth planes, uneven fracture (beryl and apatite) in the direction [0001]; (5) poor—cleavage direction is found with great difficulty (quartz, corundum). Crystals of the same substance have several directions of cleavage of similar or different degree of perfection.

Hardness of crystals is of great practical importance, especially for the abrasives industry; it is also an important diagnostic feature helpful in the recognition of minerals. It is one of the properties with respect to which crystals are strongly anisotropic. The evaluation of hardness greatly depends on the method by which it is determined. Below we discuss the principal methods of determination of hardness.

Scratch method. If one crystal scratches another, i.e., leaves a trace on it, then obviously one is harder than the other. If both crystals scratch one another, they are considered to have equal hardness. The mineralogist Mohs evolved a special scale of ten standard minerals with hardness increasing from one (the softest mineral) to ten (the hardest mineral). Hardness is determined by the number of the mineral in the scale. If a crystal is harder than one of the standards (for instance, harder than 3) and softer than the next number (4), its hardness is expressed by the intermediate value, i.e., $3\ ^1/_2$. The Mohs scale consists of very widespread minerals (except No. 10):

1. Talc
2. Gypsum
3. Calcite
4. Fluorite
5. Apatite
6. Orthoclase
7. Quartz
8. Topaz
9. Corundum
10. Diamond

The quantitative evaluation of hardness by the scratch method is carried out with the aid of a special device called a *sclerometer*. The Zeebeck sclerometer is shown diagrammatically in Fig. 299.

A crystal k is placed on a movable block T. A steel point S is pressed against the crystal by a weight P. The block with the crystal is moved under the steel point, and the weight P is varied until the point scratches the crystal.

A sclerometer of this type has two important drawbacks: (1) it cannot be used for substances which are harder than the steel of the

point; (2) it is very difficult to determine the exact weight at which a scratch begins to appear.

The instrument was later improved by Martens: the steel point was replaced by a diamond cone of a definite angle (90°), so that a definite width of the scratch groove was established (0.01 mm).

Crystals often display considerable anisotropy when tested for hardness by the scratch method. For instance, if from some point on a crystal face segments are plotted proportional to the degree of hardness in every given direction, a closed curve will be obtained which is called a hardness curve. Fig. 300 shows such a hardness curve on the cleavage rhombohedron of calcite.

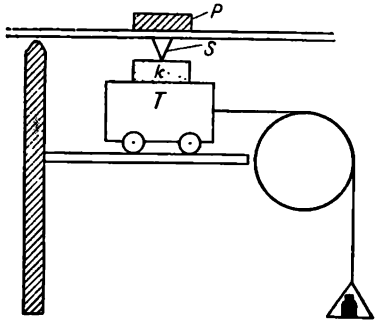


Fig. 299. Zeebeck sclerometer

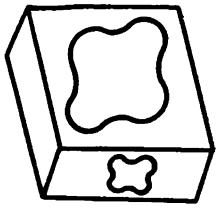


Fig. 300. Hardness indentation figure in calcite

Hardness can also be determined by the *grinding method.* A crystal is placed on a cast iron or glass disc and is ground with powdered carborundum, CSi—a substance of great hardness; both the crystal and the powder are previously weighed. Grinding is carried to destruction, which is a rather inaccurate criterion. The hardness of the crystal is determined by the loss of weight.

Minerals are also tested for hardness by an indenting method with the aid of a *microhardness tester.*

The indenting tool is a diamond pyramid square in section with an angle of 136° between opposite faces. The weight applied varies from 2 to 200 kg. The hardness number is expressed in kilograms per square millimetre. Measurement is taken along the indentation diagonal. The instrument is connected to a conventional biological microscope which gives a 400-fold magnification and has a lamp for work in reflected light. The microscope stage is so arranged that after rotation through 180° the object under the objective is placed exactly under the weight terminating in the diamond pyramid. Hardness tests can be conducted on minerals of any Mohs number.

We can see from Table 18 that the increase in the hardness of standard minerals from one number to another is far from uniform.

The most insuccessful standards are calcite, fluorite, and apatite which differ but little from each other in hardness. Notable is the hardness of diamond which is 140 times greater than that of its neighbour, corundum.

Table 18

Comparative values obtained by the sclerotic and grinding methods

Mineral	Relative hardness measured with	
	sclerometer	grinding method
Talc	2.3	0.03
Gypsum	9.5	1.25
Calcite	22.5	4.5
Fluorite	25.5	5
Apatite	35.5	6.5
Orthoclase	108	37
Quartz	300	120
Topaz	450	175
Corundum	1,000	1,000
Diamond	—	140,000

The surface graph for hardness cannot be drawn in the form of an ellipsoid.

Only two general postulates can be given for the causes of different hardness of crystalline bodies.

1. All other conditions being equal, hardness depends on the interplanar spacing—the smaller the spacing, the greater the hardness.
2. Hardness increases with valency (see Table 19).

Table 19

Hardness of NaF, MgO, ScN, TiC *

Chemical composition	NaF	MgO	ScN	TiC
Valency of ions	1	2	3	4
Interplanar spacing in the direction (100), Å	2.31	2.10	2.23	2.23
Hardness on Mohs scale	3.2	6.5	7.8	8.9

* All these substances have the structure of the sodium chloride type.

Elasticity. Alteration in the shape of a body, caused by some reason or another, is called *deformation.*

External mechanical forces applied to a crystal cause deformations which can be plastic or elastic in nature.

If a force P does not exceed a certain limit, the cessation of the action of this force is followed by the disappearance of the deformation. Such a deformation is *elastic.*

Elasticity is that property of solids by virtue of which they recover their former shape and dimensions when external forces cease to act.

The force P can be increased to a value after which a body will not recover its former dimensions completely, and some deformation will remain. Such a deformation is called *permanent* or *plastic.*

The *elastic limit* is the maximum stress intensity $(\frac{\sigma}{s})$ which leaves no permanent deformation.

Of the types of plastic deformation we shall briefly discuss gliding, and mechanical twinning.

Gliding consists of parallel translation of crystal layers along one constant (stationary) plane called the *glide plane.* The translation of individual layers is directly proportional to their distance from the glide plane. In gliding, the particles of a crystal retain their mutually parallel orientation.

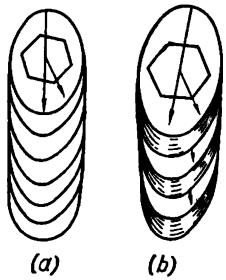


Fig. 301. Gliding in a zinc crystal:
(a) crystal before deformation; (b) crystal after deformation

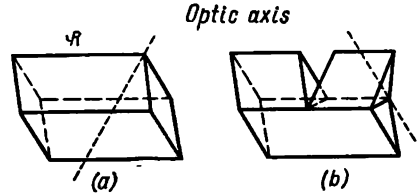


Fig. 302. Gliding in a calcite crystal:
(a) crystal before deformation; (b) crystal after deformation

A crystal of zinc may be used to illustrate the point. A cylindrical crystal (Fig. 301) elongated parallel to the axis loses its original shape and becomes somewhat flattened in the direction of gliding (small arrows in Fig. 301).

In *mechanical twinning* there is also some translation of layers along the twin plane, but in this case it obeys some law of twinning and particles change their orientation.

Mechanical twinning is characteristic of many crystals, for example, of calcite. Pressing a knife blade to one of the edges of a

cleavage rhombohedron R (Fig. 302) will produce twinning of the crystal parallel to the plane of the form $\{01\bar{1}2\}$.

When graphically represented, the elastic properties of crystals produce intricate surfaces, as can be seen from Fig. 303 showing the surface of elasticity of barite (orthorhombic system).

In 1675 Robert Hooke formulated the following law (which was named after him) for isotropic bodies: *deformation of a solid is proportional to the stress producing it.*

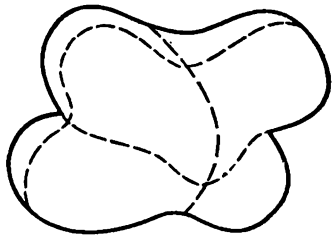


Fig. 303. Elasticity surface of barite

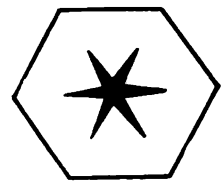


Fig. 304. Percussion figure on mica

In the case of extension Hooke's law can be expressed mathematically as follows. If the original length of a body is called L, its cross-section S, and the elongation produced ΔL, then the elongation per unit length (relative elongation) will be

$$\frac{\Delta L}{L} = \varepsilon.$$

The tensile stress (i. e., the load per unit cross-sectional area of the rod) is

$$\frac{P}{S} = \sigma.$$

Hooke's law, in the case of extension, will appear as

$$\varepsilon = \sigma e, \qquad (1)$$

i.e., relative elongation is directly proportional to the tensile stress. The number e is called the coefficient of linear extension (or compression). Its reciprocal $E = \frac{1}{e}$ is called the *modulus of elasticity* or the Young modulus. Rewriting the equation (1) with E we shall have

$$\sigma = E\varepsilon. \qquad (1')$$

If ε is unity, E in this case will be equal to σ_1. It means that the modulus of elasticity of a substance is numerically equivalent to

the stress required to extend a rod to double its original length, because when

$$\varepsilon = 1, \text{ then } \frac{\Delta L}{L} = 1, \text{ and } \Delta L = L.$$

A few words should be said about the so-called *percussion figures* which are sometimes used as diagnostic features in a rough recognition of a mineral.

If the point of a metal rod is placed on a crystal plate and the other end of the rod is struck with a hammer, fractures will appear around the point running always in the same directions depending on the symmetry of the crystal. These fractures are called percussion figures and serve as diagnostic features.

Fig.304 shows a percussion figure on the face (001) of mica—a monoclinic pseudohexagonal mineral.

THERMAL PROPERTIES OF CRYSTALS

Heat conductivity of crystals was first studied by Sénarmont in 1847. Different faces of a crystal or plates cut from it were covered with a thin layer of wax. Heat was conducted through a wire which was insulated with asbestos to prevent radiant heat from melting the wax. The wire was wrapped in asbestos, only its free end contacting the crystal through a hole in an asbestos sheet.

The wax melted at the point of contact, and in most cases the melted area was in the shape of an ellipse. If the test was conducted on a pinacoid (001) or (0001) of a crystal belonging to an intermediate system, the melted area was in the shape of a circle.

The heat conductivity properties of different crystals are clearly similar to their optical properties. The heat conductivity surface of optically uniaxial crystals has the form of an ellipsoid of rotation. For optically biaxial crystals, i.e., crystals of the orthorhombic, monoclinic, and triclinic systems, the surface of heat conductivity has the form of an ellipsoid with three unequal axes. It has two cross-sections in which heat conductivity is propagated in a circle, similarly to two circular sections of optically biaxial crystals.

As regards their thermal properties crystals are rather strongly anisotropic. The heat conductivity of some crystals may be 3 to 4 times higher in some directions than in others. It is usually higher than that of amorphous substances of the same chemical composition. This difference decreases with an increase in temperature.

Eucken has established the following laws governing heat conductivity.

1. Crystals usually have a higher heat conductivity than amorphous substances of the same composition.

2. The heat conductivity of crystals is approximately inversely proportional to absolute temperature (T). The heat conductivity of amorphous bodies decreases with decreasing absolute temperature.

3. The more complex the chemical composition of a crystal, the lower its heat conductivity.

Apart from this, Jeannetta arrived at the following empirical conclusion: the heat conductivity of crystals is much higher in the directions parallel to cleavage, than in those perpendicular to it. The data of Table 20 illustrate the above statements.

Table 20

Coefficients of heat conductivity for quartz and quartz glass

Temperature, °C	Coefficient of heat conductivity, cal/cm sec deg		
	Quartz		Quartz glass
	parallel to cleavage	perpendicular to cleavage	
100	0.021	0.013	0.0046
0	0.032	0.017	0.0033
—78	0.047	0.024	0.0028
—190	0.117	0.059	0.0016

The coefficient of thermal expansion of crystals also varies with direction, sometimes rather abruptly. In some very rare cases even compression is observed during heating, e.g., in calcite, in the directions perpendicular to the principal axis.

ELECTRICAL PROPERTIES OF CRYSTALS

The *electrical conductivity* of crystals, in contrast to that of amorphous bodies, varies with direction. There are two kinds of electrical conductivity—*ion conductivity*, which is inherent in solutions, and *electron conductivity* (in metals).

Resistivity of quartz (a dielectric) in the direction of the principal axis is hundreds of times lower than in the directions perpendicular to it. Resistivity increases considerably with an increase in temperature. The resistivity of metals also varies with direction, but the variations are negligible. The increase of temperature has less effect on metals than on non-conducting crystals.

Of great interest are the *pyroelectric* and *piezoelectric* properties of crystals. These properties have acquired a considerable industrial importance.

Pyroelectricity consists in the following. If a crystal is transferred into an environment with a temperature differing from that in which it was kept prior to the test, some of its faces become electrically charged. This phenomenon is observed only in dielectrics. It was first discovered in tourmaline which has the $L^3 3P$ symmetry (Fig. 305). The pole which develops a positive charge with an increase in temperature is called the *analogous pole* (+), the opposite one being the *antilogous pole* (—).

Pyroelectrical phenomena can be investigated by several methods. The simplest is the dusting method. A crystal is dusted with a finely powdered mixture of equal volumes of flowers of sulphur and red lead. In their passage through the silk sieve of a pulverizer the particles of powder become charged by friction, the sulphur receiving a negative charge, and the red lead a positive one. The particles are attracted and retained by those parts of the crystal which have the opposite charge. The distinct difference in the colouring of particles enables us to detect easily the presence of pyroelectricity on tourmaline crystals.

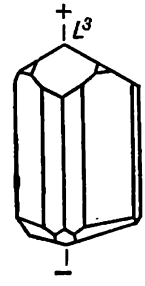


Fig. 305. Positive and negative charges in a tourmaline crystal

The quantity of pyroelectricity can be measured with the aid of a very sensitive electrometer.

Pyroelectricity is displayed only by crystals with *special* polar axes, i.e., such axes which have no congruent or reflection equivalents. *Polar* axes are axes whose opposite ends cannot be placed in a congruent position by any element of symmetry of the crystal. Special polar axes, and consequently pyroelectrical phenomena, are possible only in the following ten crystal classes: L^1, L^2, L^3, L^4, L^6, P, $L^2 2P$, $L^3 3P$, $L^4 4P$, $L^6 6P$.

Pyroelectricity is very pronounced in crystals of tourmaline belonging to the $L^3 3P$ class (Fig. 305) and of tartaric acid belonging to the L^2 class (Fig. 306).

Electrical charges may also develop in some parts of crystals of dielectrics subjected to mechanical pressures, which may be either positive (extension) or negative (compression). In both cases opposite charges will develop at the same spot of the crystal. This is called a *direct piezoelectric effect*. It has also been found that in an electric field the crystal will suffer elastic deformation, i.e., will be extended or compressed. This is called a *reverse piezoelectric effect*.

The charges develop at the ends of axes which have a polar development. Therefore, piezoelectric effects, both direct and reverse, can appear only in crystals without a centre of symmetry, i.e., in those which belong to one of the following classes: L^1, L^2, L^3, L^4, L^6, L_4^2, P, $L^2 2P$, $L^3 3P$, $L^4 4P$, $L^6 6P$, $L^3 P$, $3L^2$, $L^3 3L^2$, $L^4 4L^2$, $L^6 6L^2$, $L_4^2 2L^2 2P$, $L^3 3L^2 4P$, $3L^2 4L^3$, $3L^4 4L^3 6L^2$, $3L^2 4L^3 6P$. The last class but one does

not count because all piezoelectric constants corresponding to it are zero.

Both the direct and the reverse piezoelectric effects have been widely applied in science and engineering, principally in the measurement of pressure in a gun barrel during discharge, wavelength stabilization in radio transmitters, sounding of sea depths, transmission of directed radio signals, i.e., signals which can be received only by the particular receiver to which they are sent. Quartz and rochelle salt are the principal piezoelectric crystals used.

The intensity of the piezoelectric effect in a crystal depends on the crystallographic direction. Moreover, crystals of different substances produce effects widely differing in intensity.

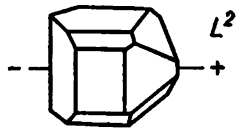


Fig. 306. Positive and negative charges in a tartaric acid crystal

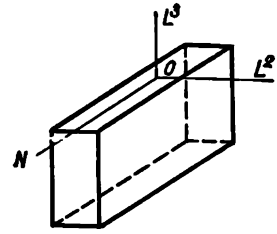


Fig. 307. A quartz plate cut perpendicularly to the electric axis

Let us discuss the following example. All the three twofold axes of quartz (symmetry $L^3 3L^2$) have polar development. If a plate in the form of a parallelepiped is cut from a quartz crystal so that some faces are perpendicular to one of the L^2 axes, which are called electric axes, and others are oriented parallel to L^3 (Fig. 307), then different charges will develop at different faces of the plate upon application of pressure. If a compression force f is applied parallel to L^2, then one of the faces normal to it will receive a positive charge, and the other a negative one.

The quantity of electricity, q, does not depend on the size of the plate, i.e., $q_{L^2} = kf$, where k is the piezoelectric constant of quartz. If the compression force f is applied parallel to L^3, no charges will develop on the faces of the plate: $q_{L^3} = 0$. If the compression force f is perpendicular to L^2 and L^3 (N in Fig. 307), opposite charges will develop on the same faces as in the first case: $q_N = k\frac{n}{b}f$, where n is the size of that edge of the plate along which the force f acts, and b is the thickness of the plate in the direction of the electric axis L^2.

MAGNETIC PROPERTIES OF CRYSTALS

In order to determine whether a substance is paramagnetic or diamagnetic it is necessary to disturb the orientation of its particles. The substance is crushed into fine powder which is placed in a glass capillary suspended by a thread in a magnetic field.

Induced para- or diamagnetism is equally strong in all directions only in singly refracting crystals. A ball made from such a crystal will occupy no definite position in a magnetic field.

Induction along the optic axis of optically uniaxial crystals will be either maximum or minimum. A ball made from a paramagnetic crystal should be so suspended that it can revolve about one of the diameters perpendicular to the optic axis. If the latter is the direction of the maximum magnetic induction, the ball will take up a position parallel to the lines of force, and conversely, if the axis coincides with the direction of the minimum induction, the ball will take up a position perpendicular to the lines of force. A ball made from a diamagnetic crystal will behave in the opposite manner.

In optically biaxial crystals the value of magnetic induction corresponds to an ellipsoid with three unequal axes. If a crystal has three elements of symmetry, the directions of magnetic induction will coincide with the principal directions of light vibrations. In crystals with one symmetry element only one direction is oriented parallel to the principal direction of the vibrations of light. In crystals of the triclinic system there is no relationship between the principal directions of magnetic and optical vibrations.

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